Capsicum annuum L. Atık Tohumlarından Elde Edilen Biyokömürün Pb(II) Biyosorpsiyon Potansiyelinin Araştırılması

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Investigation of the Pb(II) Biosorption Potential of Biochar Obtained from *Capsicum annuum* L. Waste Seeds

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ETHICAL STATEMENT

I hereby declare that this thesis study titled "Investigation of the Pb(II) Biosorption Potential of Biochar Obtained from *Capsicum annuum* L. Waste Seeds" has been prepared in accordance with the thesis writing rules of Eskişehir Osmangazi University Graduate School of Natural and Applied Sciences under the academic consultancy of my supervisor Prof. Dr. Tamer Akar. I hereby declare that the work presented in this thesis is original. I also declare that, I have respected scientific ethical principles and rules in all stages of my thesis study, all information and data presented in this thesis have been obtained within the scope of scientific and academic ethical principles and rules, all materials used in this thesis which are not original to this work have been fully cited and referenced, and all knowledge, documents and results have been presented in accordance with scientific ethical principles and rules. 19/02/2021

Mahmoud M. H. HAMMO

Signature

ÖZET

Su kirliliği, küresel endişeye neden olan önemli bir çevresel sorun haline gelmiştir ve bu sorunu gidermek için etkili bir iyileştirme yönetimine ihtiyaç vardır. Çok çeşitli biyosorbanlar arasında karbonlu malzeme biyokömürü içeren biyosorpsiyon, hem sürdürülebilir hem de uygun maliyetli bir iyileştirme alternatifi olduğu için gelecekte önemli bir fark yaratabilir. Bununla birlikte, biyokömürün çeşitli kirleticiler için biyosorpsiyon kapasitesi hakkında hala çok fazla bilinmeyen vardır ve bu tez, bu nedenle mevcut bilgi boşluğuna bilgi sağlamayı amaçlamaktadır.

Capsium annuum L. (*C. annuum* L.) tohumlarından hazırlanan yeni bir biyokömür (CASB) ile sulu çözeltilerden toksik Pb(II) iyonunun biyosorpsiyonunu araştırmak için Pb(II) iyonlarının uzaklaştırılma özellikleri denge ve kinetik yönler dikkate alınarak araştırılmıştır. Biyosorpiyon, CASB'nin 36,43 mg g^{-1} maksimum tek tabakalı biyosorpsiyon kapasitesine sahip olduğu Langmuir izoterm modelinin doğrusal olmayan formuna iyi uyum sağlamıştır. Biyosorpsiyon kinetiği ise yalancı–birinci–derece kinetic modeli ile tanımlanmıştır. CASB'nin dinamik akış modundaki biyosorpsiyon ve rejenerasyon potansiyeli incelenmiştir. Sentetik atıksu (SW) ve sentetik Pb(II) çözeltisi ile gerçekleştirilen kırılma noktası eğrisi çalışmaların yanı sıra, sürekli akış sisteminde Pb(II) eklenmiş gerçek elma suyu örnekleri kullanılarak CASB'nin uygulanma potansiyeli de test edilmiştir. Olası metal iyonu–biosorbent etkileşim mekanizması da FTIR, SEM–EDX ve Zeta potansiyel analizleri ile değerlendirilmiştir. Genel olarak, önerilen biyokömür sistemi, sulu ortamda kurşun iyonunun uzaklaştırılması için etkili bir şekilde kullanılmıştır.

Anahtar Kelimeler: Biyosorpsiyon, Biyokömür, *Capsicum annuum* L. tohumları, Modelleme, Karakterizasyon, Kurşun (II), Uygulama.

SUMMARY

Water contamination has become a major environmental problem of global concern. There is a need for effective remediation methods to counteract this problem. Biosorption including carbonaceous material biochar, among a wide variety of biosorbents can make an important difference in the future, as it is both a sustainable and cost–effective remediation alternative. However, there is still much unknown about biochar's biosorption capacity for various contaminants, and this thesis, therefore, aims to contribute knowledge to this existing knowledge gap.

In order to investigate the biosorption of toxic Pb(II) ion from aqueous solutions by new biochar (CASB) prepared from *Capsicum annum* L. (*C. annum* L.) seeds, the removal characteristics of Pb(II) ions was investigated by considering equilibrium and kinetic aspects. Biosorption was well described with a non–linear Langmuir isotherm model with the maximum monolayer biosorption capacity of 36.43 mg g^{-1}. Biosorption kinetics were well described by the pseudo–first–order kinetic model. Dynamic flow mode biosorption and regeneration potential of CASB were examined. Its application potential was also tested using real apple juice samples spiked with Pb(II) in the continuous flow system in addition to breakthrough studies carried out with simulated wastewater (SW) and synthetic Pb(II) solution. The possible metal ion–biosorbent interaction mechanism was also evaluated by FTIR, SEM–EDX, and Zeta potential analysis. Overall, the suggested biochar system was effectively used for the removal of a lead ion from contaminated solutions.

Keywords: Biosorption, Biochar, *Capsicum annuum* L. seeds, Modeling, Characterization, Lead (II), Application.

LIST OF CONTENTS

LIST OF CONTENTS (continued)

LIST OF CONTENTS (continued)

Page

LIST OF FIGURES

Figure **Page**

LIST OF TABLES

Table **Page**

LIST OF SYMBOLS AND ABBERVIATIONS

Abbreviations	**Statements**
°C	Centigrade scale
min	Minute
BC	Biochar
C. annuum L.	*Capsicum annuum* L.
CASs	*Capsicum annuum* L. seeds
CASB	*Capsicum annuum* L. seeds biochar
EDTA	Ethylenediaminetetraacetic acid
HMs	Heavy metals
AC	Activated carbon
SW	Simulated wastewater
g	Gram
M	Molar
h	Hour
DI	Deionized
b	Langmuir isotherm constant: relates to the affinity of binding sites
C_e	Equilibrium Pb(II) ion concentration
C_f	Final Pb(II) ion concentration
C_i	Initial Pb(II) ion concentration
pH	The negative logarithm of the hydrogen ion (H^+) activity
pH_{PZC}	pH of zero point charges
K_L	Langmuir equilibrium constant
K_F	Freundlich linearity coefficient
$1/n$	Heterogeneity factor, dimensionless
β	Activity coefficient related to the biosorption energy
ε	Polanyi potential
R	Gas constant
T	Absolute temperature

LIST OF SYMBOLS AND ABBERVIATIONS (continued)

t	Time
q_e	Amount of Pb(II) ion biosorbed (mg g^{-1} biochar)
t_b	Breakthrough time
t_e	Exhaustion time
R_L	Langmuir regression constant
R^2	Coefficient of determination
mg	Milligram
mL	Milliliter
µm	Micrometre
ASTM	American Society for Testing Materials
D–R	Dubinin–Radushkevich
AAS	Atomic Absorption Spectrometry
IR	Infrared Spectroscopy
EDX	Energy Dispersive X–ray
SEM	Scanning Electron Microscopy
EPA	Environmental Protection Agency
ATSDR	Agency for Toxic Substances and Disease Registry
NRC	National Research Council

1. INTRODUCTION AND PURPOSE

With the rapid growth of industries today, significant volumes of wastewater containing metal pollutants are discharged into the natural receiving water system, causing serious water pollution (Li et al., 2014). Contamination of waters with toxic metals is a global problem that causes great harm to living systems and the aquatic ecosystem. Lead is one of the emerging pollutants released into the environment by industrial effluents. It is highly toxic to living organisms, even if it is very low concentration (Kadimpati, 2017; Morosanu et al., 2017). Long–term lead exposure was investigated to cause an increase in blood pressure, as well as anemia, and that especially in middle– and old–aged people. Serious damage of brain and kidney of both adults and children is related to exposure to high lead levels that causes to death. Moreover, the toxicity of lead can cause serious damage to the nervous system (Canfield et al., 2003; Bhatnagar, 2006; Wani et al., 2015).

For these reasons, various treatment methods are used to remove Pb(II) ions from polluted waters. Those methods include precipitation, ion exchange, membrane separation, reverse osmosis, evaporation, electrochemical treatment, and filtration. However, the presence of low concentrations of Pb(II) ions in wastewater makes these traditional processes expensive and ineffective. Also, waste sludge occurred in these methods is a secondary problem (Verma et al., 2016). Biosorption was defined by Volesky (2007), as the property of some biomolecules (or biomass types) for binding and concentrating selected molecules or other ions from aqueous solutions. This process is still developing in our time but has shown its effectiveness in water and wastewater treatment. Research in this area continues to discover new materials to apply in this process, and these materials are highly appreciated by the researchers for their environmentally friendly and economical properties (Al-Wakeel et al., 2015; Golie and Upadhyayula, 2017).

To remove heavy metals, a wide range of biological materials was investigated which are low–cost, available and sustainable materials such as algae, agricultural waste, industrial waste, animal products, raw plants, and sludge (Fomina and Gadd, 2014; Feizi and Jalali, 2015; Hlihor et al., 2015; Vijayaraghavan and Balasubramanian, 2015; Zhou et al., 2015b; Malakootian et al., 2016; Lucaci et al., 2020).

In the past few years, especially in the last five years, research has increased on the topic of converting biomass into biochar and still increases over time because biochar is an environmentally friendly and sustainable material. Biochar is a carbon–rich solid material and has unique physical, chemical, and biological characteristics, for example, high pore volume, stability, wide specific surface area, enriched with functional surface groups, enormous content of minerals, and high biosorption capacity. Moreover, the raw materials of biochar production are inexpensive and obtainable in abundance, and the biochar preparation is cheap, with low energy requirements (Liu and Han, 2015; Abdelhadi et al., 2017; de Caprariis et al., 2017; Hu et al., 2017; Kavitha et al., 2018; Yao et al., 2018; Dai et al., 2019; Elkhalifa et al., 2019; Wang and Wang, 2019; Zhang et al., 2019b).

Biochar is synthesized through thermochemical processes, which include pyrolysis, hydrothermal carbonization, and gasification (Qian et al., 2015). The most popular thermochemical technique for biochar production is pyrolysis, under which breakdown of organic components in an oxygen–limited atmosphere at an adjustable temperature. Generally, the major parameters affecting products of pyrolysis are the temperature of the reaction, holding time, heating rate, and nature of feedstock (Zhang et al., 2019b). The yields of the biochar decreased with temperature increase (Xu et al., 2015).

Biomasses present in several forms, such as wood waste, agricultural residues, forest residues, municipal solid waste, and animal manure, were used as raw material for the processing of biochar (Duku et al., 2011). Biochar was used as a biosorbent and a soil modifier to uptake organic pollutants (dyes, pesticides, antibiotics, and persistent organic pollutants, etc.), heavy metals (Hg(II), Pb(II), Cd(II), Cu(II), etc.), and other inorganic pollutants (NH_4, NO^{3-}, F^-, PO_4^{3-}, etc.) from wastewater and remediate soil polluted with heavy metals and organic contaminants (Ahmad et al., 2014; Tan et al., 2015).

In this study, CASB was prepared as a new biochar by using *Capsicum annuum* L. seeds (CASs) waste as feedstock. To the best of our knowledge, it was the first attempt to employ CASs based biochar for bioremediation purpose. Pb(II) was chosen as the target highly toxic metal ion for analyzing the batch and continuous flow mode biosorption performance of CASB. Biosorption optimizations of the batch system such as initial pH value, amount of biosorbent, biosorption equilibrium time, initial metal ion concentration, also, optimizations of the continuous flow systems such as flow rate, amount of sorbent, and regeneration potential of CASB were determined. Moreover, the biosorption process was applied to real apple juice, simulated wastewater, and synthetic Pb(II) solution samples in continuous flow systems, in addition to the studies aimed at clarifying the sorption kinetics and isotherms. Moreover, IR, SEM–EDX, and Zeta potential analysis were employed to evaluate the possible interactions between CASB and Pb(II) ions. Finally, in the planned study, as an effectively, environmentally friendly, economical, and novel alternative biomaterial, CASB is presented for the uptake of Pb(II) from the contaminated aqueous media. This material could also be a model for other seeds waste–based biochar applications.

2. LITERATURE REVIEW

Biosorption is a process of sorption in which biomass or biopolymer is played a role as a biosorbents. Biosorption phenomenon was observed at the beginning of the 1970s when radioactive elements (as well as heavy metals) were discharged from a nuclear power station in wastewater (He and Chen, 2014).

Wei et al. (2018), were used Aerobic granular sludge–derived biochar in the biosorption process to estimate the Cu(II) removal performance and impact of effluent organic matter (EfOM) sorption onto biochar by applying fluorescence and batch processes. The finding was that EfOM gave an improvement by increasing the efficiency of removing the Cu(II) onto biochar. According to this study, the pseudo–second–order model and Freundlich equation were found to be the most appropriate. Humic acid (HA) and fulvic acid (FA) were two basic compounds in EfOM, and they showed a decrease in their tendency to add Cu(II), according to the implicit understanding of Spectroscopic, and this may be a reason for the explanation for the increased biosorption performance. As a result of this study, it is to give information about the meal treatment process by utilizing biochar with a deep and accurate understanding.

By Zhang et al. (2017b), as another study in the same field, used the leaf of *Leersia hexandra* Swartz (BLLH) as feedstock to produce biochar as a biosorbent and studied its efficiency to uptake Cr(VI) in the aqueous media. Functional groups of the biosorbent were investigated by FTIR spectra and were fundamentally responsible for Cr(VI) uptake. 99.65% and 24.91 mg g^{-1} were the percentage removal and the capacity of biosorption for Cr(VI), respectively. The maximum biosorption capacity of Cr(VI) was noticed as 349.81 mg g^{-1} at the initial concentrations of Cr(VI) (1000 mg L^{-1}), and the pH was 5.0. The pseudo–second–order model, and the experimental biosorption equilibrium data was suited with Freundlich isotherm. The findings of this study pointed out that BLLH may be utilized as an efficient and cheap biosorbent for the uptake of Cr(VI) from aqueous media.

In the another study, carried out by Wang et al. (2018c), Oil–tea Camellia Shells (OCS), which transformed into biochar, then biochar, $MnSO_4$, $Al(NO_3)_3$, Na_2CO_3, and NaOH were used for the synthesis of the Biochar/MnAl–layered double hydroxides (LDH) composite. For the uptake of Cu(II) from aqueous media, the composites were successfully synthesized, and this was verified by SEM–EDS, FTIR, and XRD characterizations. According to characterizations which pointed out the process of biosorption was through surface precipitation $Cu_{2.5}(OH)_3SO_4$ and between Mn(II) and Cu(II) exist of isomorphic substitution. Isotherms and kinetics studies have shown that Cu(II) biosorption onto biochar/MnAl–LDH followed the pseudo–second–order model and Langmuir model. 74.07 mg g^{-1}, which was the Langmuir maximum Cu(II) biosorption capacity of composite. The Biochar/MnAl–LDH proved that a worthy biosorbent could be applied to remove Cu(II) from wastewater, and it has a higher biosorption capacity if compared with activated carbon and modified biochar.

Wang et al. (2018a), worked on slow pyrolysis biochars that were prepared from different three types of biomasses such as bamboo chips, hickory chips, and peanut hulls and pre–treated with eggshell waste for the uptake of lead ion from the aqueous media and these biochars revealed that relatively fast kinetics of biosorption to lead ion in aqueous solutions. Non–linear Langmuir model was used to depict the biosorption isotherms as maximum capacities of biosorption for Pb(II) (103–261 mg g^{-1}) and these values are higher compared to the original biochars which are (32.9–56.0 mg g^{-1}). The result showed that composite materials of biochar that was treated with eggshell particles could be applied as a low–cost high effective technology in the water treatment and agriculture sector.

Biosorption of cadmium (Cd) was investigated as a function of several factors such as pH, biosorbent dosage, initial concentration of Cd(II), and microalgal–biochar ratio by (Shen et al., 2017), using modified biochar using microalgal (*Chlorella* sp.)–biochar immobilized complex (MBIC). Equilibrium data fitted Sips model, and the maximum biosorption capacity was 217.41 mg g^{-1} with a *Chlorella* sp.: biochar ratio of 2:3. The kinetic model of the biosorption process of MBIC was better fitted the equilibria as pseudo–second–order equations ($r^2 > 0.999$). Characterization of the MBIC was investigated by using Zeta potential, SEM, and FTIR, which revealed that the major mechanisms to uptake Cd were the ion exchange, electrostatic attraction, and surface complexation.

The removal of Pb(II), Cd(II), Ni(II), and Co(II) in aqueous media was achieved by (Mosa et al., 2017), utilizing chemically modified biochar (CMB) derived from *Cotton stalks*. Various chemical pre–treatments of biochar with different mineral/organic acids, such as oxalic acid (OAB), sulfuric acid (SAB), sodium hydroxide (SHB), and the untreated biochar (UTB) in the batch biosorption experiments were studied to estimate their removal efficiency of these ions. The characterization of the CMB surface was performed using FTIR spectroscopy and SEM–EDS. The most effective product for biosorption of Pb(II) was with SHB (44.64 mg g^{-1}), Cd(II) (0.648 mg g^{-1}), and Ni(II) (6.20 mg g^{-1}) but, UTB presented the highest biosorption capacity of Co(II) (0.522 mg g^{-1}). The results proved the importance of the chemical treatment of biochar and its effect on the efficiency of biosorption.

In their paper Abdelhadi et al. (2017), biosorption of a mixed solution of Cu(II), Pb(II), Cd(II), Ni(II), and Zn(II) have been studied at 50 ppm as a final concentration and pH 5.2 from water by biochars derived with a surface area of 1.65–8.12 m^2 g^{-1} which were prepared from olive mill solid waste (OMSW). The authors have used mixed (Whole) of two olive cultivars (Picual, Souri) as biomass and two processes for producing oil (two–or three–phase) with varied parameters, which included different pyrolysis temperatures (350°C or 450°C) for five hours. Picual residue from the technique of two–phase milling, pyrolyzed at 350°C was the highest heavy metals (HMs) uptake capacity with more than 85% compared to other types of biochar and commercial activated carbon. The result showed that the presence of cellulose remains in biochar, a major functional group for the removal of the above four ions.

Biosorbent's potential to remove toxicity of Cu(II) from aqueous solution by sunflower seed husk biochar (SSHB) was carried out by (Saleh et al., 2016). The batch experiments were conducted at 298, 303, and 308 K, with different time intervals until 96 h. At all examined temperatures, the SSHB showed the best biosorption in the removal process of Cu(II) compared with sunflower seed husk feedstock (SSHF) and activated carbon (AC). Investigation of functional groups of the SSHF was conducted using FTIR, which revealed that it has higher surface reactivity than SSHF and AC. SSHB was not affected by the temperature of reaction and time in their removal capacity for Cu(II), while SSHF and AC were affected by these parameters. The kinetics of biosorption was carried out, and the data matched with pseudo–second–order with an r^2 value of 1 and 0.999. The results showed that SSHB as new efficient, a cost–effective, and active biosorbent for remediation drainage water.

Biosorbent, like *Sesame straw* biochar (SSB), was used to investigate competition in the biosorption between different toxic heavy metals in mono and multimetal forms by (Park et al., 2016), in aqueous solution. It was observed that maximum uptake capacity (mg g^{-1}) of heavy metals in the mono form was recorded Lead (102) >> Cadmium (86) >> Chrome (65) > Copper (55) >> Zinc (34) and in form of multimetal Lead (88) >> Copper (40) >> Chrome (21) > Zinc (7) ≥ Cadmium (5). The behaviors for models of biosorption and simulation by three–dimensional was not similar in mono and multimetal biosorption because there is a competition. In order to reach an accurate estimate of the biosorption capacity of the biochar for heavy metals in natural environments, competitive biosorption must be studied. The result showed that *Sesame straw* biochar was presented as a potential biosorbent and reduced the heavy metals toxic effect in aqueous solution.

Orange peel biochar (OP–BC) and sugar cane biochar (SC–BC) were prepared by the pyrolysis at low temperature (< 500°C) and utilized as biosorbents for the removal of Pb(II) ions from aqueous media by (Abdelhafez and Li, 2016). The batch biosorption, according to this paper, was depending on the function of pH, contact time, initial concentration of Pb(II) ions, and temperature. Biochar characterization performed using an FTIR analysis showed that the presence of hydroxyl, carboxyl, and carbonyl groups is responsible for biosorption of lead (II). It was observed that among these two biochars, SC–BC had a high surface area, so it was more effective than OP–BC and had a higher removal capacity in mg g^{-1} of Pb(II) ions 86.96 and 27.86 mg g^{-1}, respectively. Equilibirum data was described by the Langmuir model and biosorption kinetics with pseudo–second–order kinetic model as best followed. The results indicated that those two biochars have fast and high biosorption capacities in the removal of lead ions in the aqueous media.

As novel treated biochar, the batch biosorption experiments was applied in order to investigate the biosorption of Pb(II), Cu(II), and Cd(II) via $KMnO_4$–treated *hickory wood* by (Wang et al., 2015), to improve the efficiency of the biosorption. MnO_x ultrafine particles have covered the surface of engineered biochar, as shown by characterization experiments. It was found that the biosorption capacity of the engineered biochar significantly increased via pre–treatment with $KMnO_4$ in comparison with the pristine biochar and showed maximum biosorption capacity for Pb(II), Cu(II), and Cd(II) as 153.1, 34.2, and 28.1 mg g^{-1}, respectively. The result showed that the biosorption significantly increased with pre–treatment process.

Lee et al. (2015), have demonstrated that the heavy metal (Pb(II), Cu(II), and Cd(II)) biosorption capacity of Peat moss can be increased after converted to Peat moss–derived biochars by the pyrolysis at 800°C for 90 min as optimum carbonization condition which was the most effective for the uptake of Pb(II) and Cu(II). Kinetics of the process were assessed, the pseudo–second–order well–fitted, and also isothermal information was very well described by Langmuir isotherm. The maximum biosorption capacity was observed for Pb (81.3 mg g^{-1}), then by Cd and Cu, that was 39.8 and 18.2 mg g^{-1}, respectively. Hence, peat moss–derived biochar can be used as a new, cost–effective biosorbent in the treatment of heavy metal–contaminated water.

Studies using the biochars as biosorbent prepared from Sugarcane bagasse at 250, 400, 500, and 600°C were reported by Ding et al. (2014). The biosorption kinetics, isotherms, and desorption of lead ion were surveyed. All biochars were efficient in lead biosorption and well–characterized by the Langmuir isotherm model and pseudo–second–order kinetic model. The maximum Pb(II) biosorption capacity decreased from 21 to 6.1 mg g^{-1} when the temperature increased from 250 to 600°C. The responsible for the high lead biosorption onto low–temperature biochars (250 and 400°C) may that from functional groups of oxygen and as shown the FTIR analyses and kinetic models, while low lead biosorption on high–temperature biochars (500 and 600°C) was mainly responsible for intraparticle diffusion. The temperature of pyrolysis significantly impacted biochar characteristics and played a vital role in the mechanisms and capacity of lead biosorption onto biochars. Bagasse biochar was able to work as a potential alternative for the uptake of toxic lead ions from aqueous media.

Spartina alterniflora derived biochar (SABC), natural, cost–effective biochar was used for the uptake of Cu(II) ion in aqueous media by (Li et al., 2013). The low temperatures (≤ 500°C) under no oxygen conditions were optimum temperatures for pyrolysis of biomass with optimum pH range 5.5–6.5 until arrived at high biosorption affinity for Cu(II). Biosorption of Cu(II) onto SABC was detected and fitted well with the Langmuir isotherm and pseudo–second–order kinetic model. The Cu(II) biosorption capacity of SABC reached maximum value at 48.49 mg g^{-1}, which is almost five times higher than the biomass feedstock.

3. HEAVY METALS AND THEIR EFFECTS

Increased environmental contamination and the damage of ecosystems was due to the increase in industrial processes that assisted in accumulating pollutants as for example synthetic compounds, toxic metals, nuclear waste liquids, etc. (Veglio and Beolchini, 1997), and the important environmental problem is heavy metal pollution and their toxic effect (Malik, 2004). "Heavy metals such as cadmium, lead, zinc, chromium, copper, etc., are toxic even at low concentrations" (Volesky, 2003). Priority has been given to heavy metals in the surface and groundwater as major inorganic pollutants in the environment due to their motility in natural aqueous ecosystems (Atkinson and Bux F, 1998).

3.1. Sources of Heavy Metals in the Environment

The modern industries are quite responsible for the pollution of the environment. Bodies of water are being inundated with the waste matter and toxic materials, especially heavy metals, which reach serious levels (Vieira and Volesky, 2000). Metals can either be revealed in their elemental state, which means that they are not passed to further biodegradative operations or restricted in different salt complexes. In either case, metals cannot be mineralized (Atkinson and Bux F, 1998).

The biggest threat to the environment is heavy metal pollution from various sources such as agrochemicals, ballast water, electronic waste, vehicle exhaust, industrial effluents, coal power plants, sludge waste, medicinal chemicals, laboratory waste, and domestic waste. But in general, the sources of heavy metals in the environment were divided into two sources: anthropogenic and natural sources (He et al., 2013).

In comparison with natural sources, anthropogenic sources are widely considered to be the major causes of the increasing pollution of heavy metals in the environment (He et al., 2013). Some sources of heavy metals are given Figure 3.1 (Kumar et al., 2016).

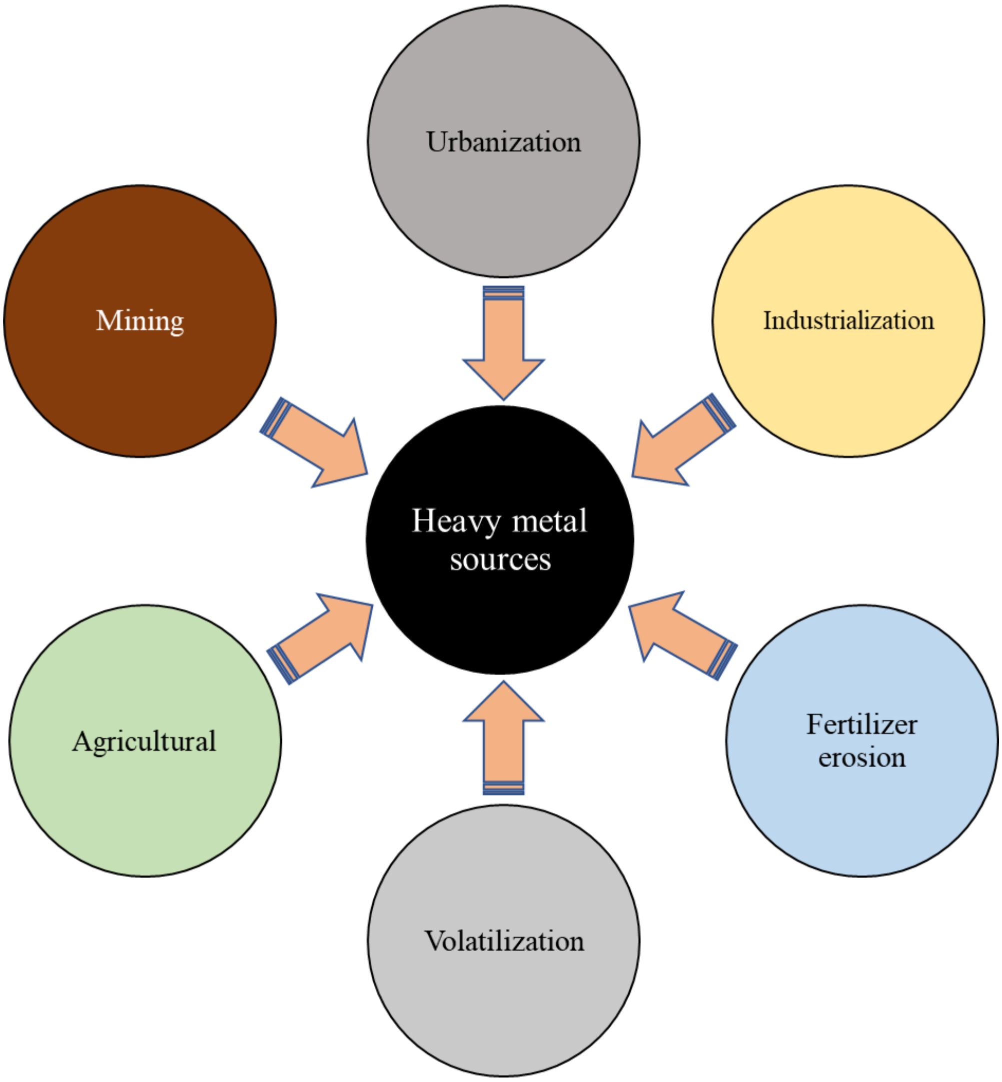

Figure 3.1. Source and sink of heavy metals

About their occurrence, mining contributes the most, while urbanization contributes the least source of heavy metal in a developing country's waste products (Kumar et al., 2016).

There are natural sources of heavy metals. Natural sources are including volcanoes, degradation of minerals and forest fires, evaporation from soil and water surfaces. Natural emissions of heavy metals must be regarded to be part of the local and global environment (He et al., 2013).

3.2. Heavy Metals Effects on Living and Environment

The harmfulness of heavy metals relies on their chemical shapes. Research suggests that the organic Hg compounds, particularly methylmercury, are more harmful than inorganic Hg. On the opposite, organic As species are less harmful than inorganic As compounds (He et al., 2013). Because of its toxicity and mutagenicity, heavy metals play an important role in the environment between pollutants. The lead(Pb), zinc(Zn), cadmium(Cd), chromium(Cr), copper(Cu), aluminum(Al), and mercury(Hg) are the most common toxic heavy metals (Agwu et al., 2018). Figure 3.2 representation depicting the impact of heavy metal on the environment and organisms (Farcasanu et al., 2018).

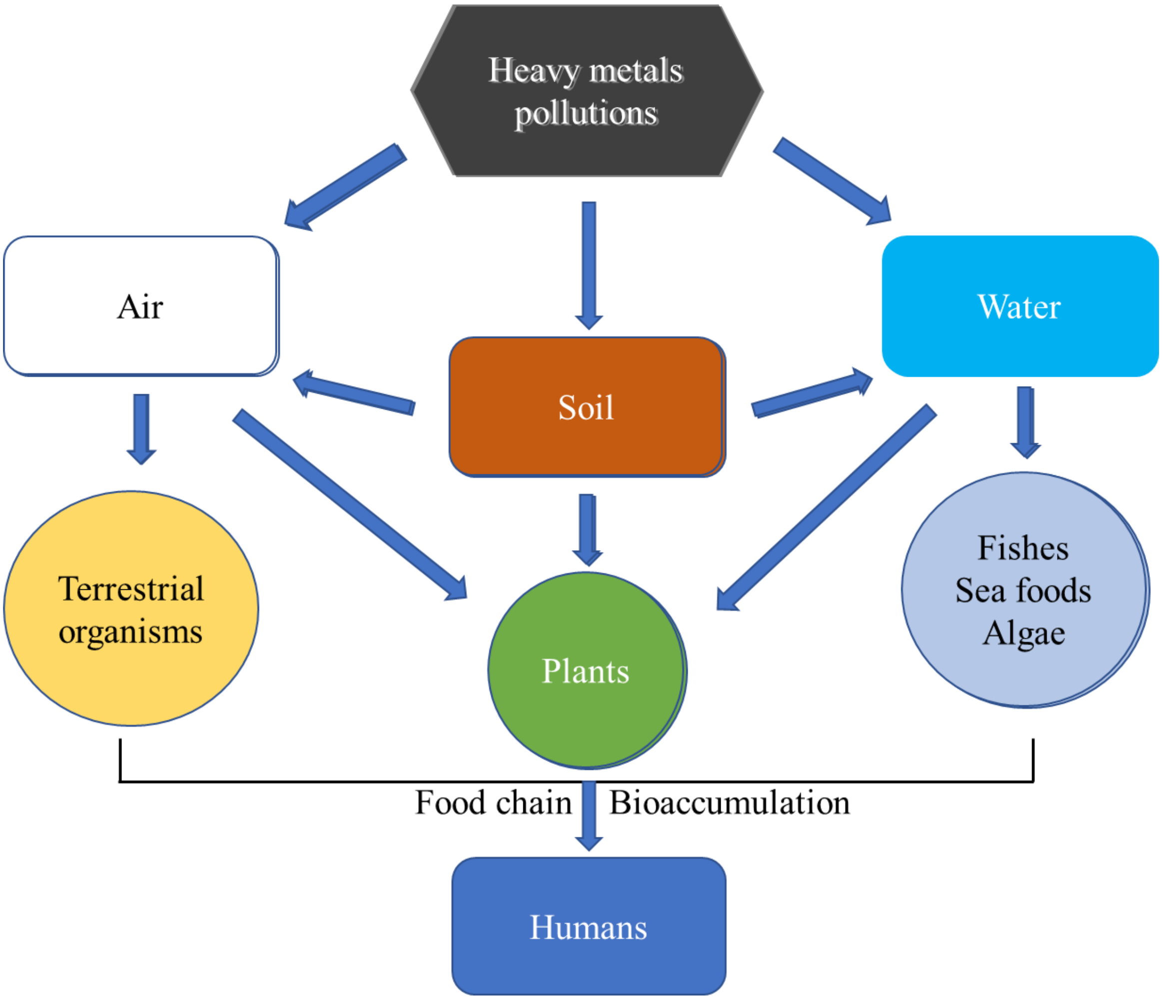

Figure 3.2. Impact of heavy metal on the environment and organisms

Toxicological research appears that heavy metals a risk to human health, animals, and plants Al Hawari (2004). Heavy metals can not be biodegraded, and they can be stacked in living tissues, causing different maladies and disturbances. In wastewater, heavy metals will adversely affect humans, animals, and plants. In the aqueous phase, long–term heavy metals exposure may pose significant health hazards even at low concentrations (Ahmed et al., 2016).

These metals may come to the body through different paths such as a dermal or inhalational path or by ingestion of heavy metals either through polluted nourishment and/or drinking water. In fact, heavy metals react with certain compounds of the body like oxygen and chloride and exhibit their toxic effects (Rusyniak et al., 2010). Continuously facing of the body with heavy metals may lead to an internal imbalance in the body. When these metals begin to accumulate in the body, the body begins to use them as an alternative to the basic elements. For instance, calcium replaced by lead, zinc replaced by cadmium, and the majority of trace elements is replaced by aluminum (Rehman et al., 2018). Furthermore, stored heavy metals devastate major metabolic processes of the body, as well as creating antioxidant imbalance. Likewise, the activity of different hormones and basic enzyme’s function are also affected (Mukke and Chinte, 2012). Changes in carbohydrate, lipid, and protein metabolism increased the body's sensitivity to infection (El-Safty et al., 2009). All of these processes finally change the neurotransmitter synthesis and its use in the body, thus changing the operations of the Central Nervous System (CNS) (Hyder et al., 2013).

Low concentrations of heavy metals like Zn, Ni, Cr, and Cu are essential micronutrients for animals, plants, and microbes. Moreover, certain heavy metals are considered to be significant toxicants to all types of living organisms at a high level. Heavy metals, for instance, Pb, Cu, Cd, Cr, Ni, and Zn, are the most popular biosphere contaminants and are the source of serious effects such as carcinogenicity, cytotoxicity, and their wide interaction mutagenicity (Rehman et al., 2018). High levels of those toxic heavy metals, especially influence cell organelles and components involved in regular cell processes, DNA–cell damage mends, and overlaps with main metabolic processes (Oves et al., 2013). Heavy metals cause different health hazards, for instance, damage to the kidneys, cancer, cognitive disorder, diseases of the heart, allergy, and irritations of the skin, and anemia as chronic disorders in the neurological system and brain. In addition, humans may be exposed to the danger of heavy metals directly exposed to contaminated air, soil, or water (Järup, 2003; Gopinath et al., 2020).

For instance, Cr(VI) is very toxic, and the ability to cause cancer has been investigated through its ability to destroy DNA and mutations (Cohen et al., 1993). Large amounts of drainage waters and residues (that including Cr) were released from industries that utilize chromium as feedstock material, like in the process of extracting a metal in its pure state, electroplating systems, paint, and leather (Gode and Pehlivan, 2007; Zhang et al., 2017b). Chromium negatively affected the growth of micro–organisms (Shakoori et al., 2000) as well as higher plants (Davies Jr et al., 2002). Chronic exposure of Cr in humans and animals leads to chromium ulcers, allergic dermatitis, and nasal septum perforation (World Health Organization, 1988).

Cadmium(Cd) is an unessential element for living beings, and extensively found within the sewerage of the mining, electroplating, smelting, re–chargeable batteries and different manufactures. It is carcinogenic even at relatively small doses (Sarı and Tuzen, 2008; Vimala and Das, 2009; Parab et al., 2010; Chen et al., 2014).

Nickel(Ni) is a required element of the human body in order to produce red blood cells. Nevertheless, exposure of the body to large quantities of it can lead to losing the weight, damage of the heart, skin, and liver (Veera, 2013). The major sources of nickel contamination have been found in power stations and waste combustion installations (Kadali, 2013).

3.3. Mutagenic and Carcinogenic Metals

Mutagenicity is the capacity of a physical, chemical, or biological agent to generate changes in heritability (mutations) in the genotype in a cell as a result of changes or loss of genes or chromosomes (or portions thereof) (Duffus and Worth, 1996).

3.4. Lead and Effects

Lead (Pb) is not only a non−essential element for plants, but also a contaminant for soil; it can enter plants and then the human body Jaishankar et al. (2014). Nevertheless, anthropogenic activities result in the highest concentrations in nature. Both of its chemical and physical characteristics such as smoothness, flexibility, weak conductibility, ductility, and resistance to erosion, man usages have favored the lead and its compounds from ancient times for a wide range of requests. The first usage of lead was the Romans on a widespread in the production of pipelines for water supplies, make of dishware and kitchen utensils, or indeed as a pigment. Lead harming was exceptionally vital from the 16th to 19th centuries as a result of its broad utilize in pottery, pipelines, shipbuilding, windows manufacture, the industry of dyes, arms, and printing of books (García-Lestón et al., 2010).

3.5. Routes of exposure to lead and its sources

Exposure of mankind to natural lead was limited prior to the manufacturing revolution but has expanded with manufacturing and large−scale mining. Lead pollution of the environment is high in comparison to that of other trace elements (Flegal and Smith, 1992). In the last 5,000 years, the amount of polluting lead discharged into the environment closely parallels the record of lead production. About half of the lead generated is released as contamination into the environment (NRC, 1980).

There are many pollution sources of lead, especially battery waste, fertilizers and pesticides, metal plating and finishing operations, exhaust from automobiles, gasoline additives, automotive pigment, and ores smelting (Baby et al., 2019).

3.6. Lead toxicity and consequences

The International Agency for Research on Cancer has categorized lead as a potential (group 2B) human carcinogen and its inorganic compounds as possible (group 2A) human carcinogens. Among all the organs, the nervous system is the most influenced objective in the toxicity of lead, both in adults and kids. Also, the reproductive system is affected by its toxicity. However, toxicity in children is more influential than in adults. It is because their internal and also external tissues are softer than they are in adults. Long–term adult exposure may result in reduced performance in some cognitive ability tests that evaluate nervous system functions. Long–term lead exposure was investigated to cause an increase in blood pressure, as well as anemia, and that especially in middle– and old–aged people. Brain and kidney seriously damaged, for both adults and children, were discovered is related to exposure to heavy lead levels that lead to death (Canfield et al., 2003; Bhatnagar, 2006; Wani et al., 2015).

Exposure of lead can impact children as well as adults, but children who will experience symptoms are the biggest concern at substantially lower rates of blood lead levels (BLLs) than adults. Measuring lead in blood is the most widely used indices of lead exposure (Chen et al., 2012a).

4. INDUSTRIAL WASTEWATER AND HEAVY METALS REMOVAL METHODS

4.1. Heavy Metals in Industrial Wastewater and Their Properties

Water is an indispensable component of life. Water pollution has been defined as contaminated water due to a change in its chemical, physical, or biological properties. It is said that water is polluted when it's quality or composition changes either by nature or as a result of human activities. It thus becomes unsuitable for domestic, industrial, agricultural, and recreational usages and wildlife survival (Srinivas, 2008). Global warming and the expanding world populace will put an increased stretch on the water and agricultural supply systems. Industrial development and its activities contaminate these resources and diminish the capacity in the future (J Binkley and Simpson, 2003).

The existence of rapid urbanization, industrialization, and population growth to which the global environment is exposed has put an end to the use of limited natural resources. These factors have increased the levels of toxic heavy metals nearly everywhere. Most of the manufacturing activities include leakage and redistribution of heavy metals such as metalliferous smelting, mining and electroplating, iron and steel, metallurgy, electrolysis, leatherworking, electro–osmosis, photography, etc. (Jinsheng Sun et al., 2012). Wastewater discharged from factories by a specific industry is the effluent. The shape and type of industry, industrialization process, raw materials utilized, and housekeeping determine the quantity and quality of that polluted water. In other words, the properties of that water quite differ from industry to industry (Srinivas, 2008). Unlike contaminants of organic that can be degraded to nontoxic products, metals cannot be further transmuted or mineralized to a completely innocuous species (Doble and Kumar, 2005).

4.2. Methods for Heavy Metal Removal From Aqueous Solution

The researchers have witnessed a wide range of techniques for removing heavy metals from aqueous solution. Method selection depends on many variables, such as time, cost, ease of operation, safety, effectiveness, long–term, and short–term environmental impacts.

The heavy metal ions biosorption onto biochar can be described by the two types of biosorption processes: physical and chemical biosorption (Mahdi et al., 2018).

On the basis of both the heavy metals and properties of biochar, there are many biosorption mechanisms for removing pollutants by BCs have been suggested, involving: 1– biosorption on the surface by coordination to π electrons (C=C); 2– precipitation as an insoluble substance like hydroxide, carbonate, and phosphate; 3–ion exchange with cations; 4– surface complexation with functional groups such as free carboxyl and hydroxyl; and 5– electrostatic interactions (Cao et al., 2009; Uchimiya et al., 2010; Harvey et al., 2011; Lu et al., 2012; Kılıç et al., 2013).

4.2.1. Adsorption

Among the different techniques for the treatment of water, the adsorption treatment is an appealing approach for water treatment, especially in case the adsorbent is cheap and does not require a pretreatment stage before its application (Bande et al., 2008). This method has been demonstrated for numerous applications to be prevalent to other methods for many reasons (Kargi and Özmıhçı, 2002; Bohdziewicz and Sroka, 2005; Li et al., 2011) including the simplified design, low cost, efficiency of removal high, easiness of operation, and availability. Furthermore, this process can remove/minimize the various type of pollutants, and in this way, it has a variety of applicability in water contamination control (Gupta and Ali, 2012). Without a doubt, activated carbon classed as an international adsorbent for effluent remediation and is very often used for the removal of diverse pollutants from water (Zhang et al., 2011). Textural properties of activated carbon, and surface chemistry, are the main parameters to create their adsorption capacity for specific pollutant (Jaramillo et al., 2009; Saucier et al., 2015; Zhou et al., 2015c).

4.2.2. Chemical precipitation

It is an efficient technique for heavy metal uptake from wastewater. In this process, there is an interaction between chemicals and the heavy metals existent in wastewater, and there is the creation of insoluble precipitates. Chemical precipitation has categorized as hydroxide precipitation and sulfide precipitation (Renu, 2017).

Actuality, a popular method for metal removal is pH precipitation. The pH−adjusted for polluted water until it achieves a basic value (pH 10−11). By that pH, according to (Equation 4.1), metal ions become a form of hydroxide (Jes´us S´anchez-Mart´ın and Beltr´an-Heredia, 2012).

$$M^{2+} + 2(OH)^{-} \rightarrow M(OH)_2\downarrow \qquad (4.1)$$

The heavy metals removal from drainage water by chemical precipitation is simple and low cost. It has some drawbacks such as sludge production, which needed to treat with great difficulty and also requires a considerable chemicals amount to diminish metals to a satisfactory level for discharge. This process is applicable for the case when the heavy metals concentration is high, and for low concentration of heavy metal, it is not efficient particularly when the concentration of a metal ion in aqueous media is less than 100 mg L^{-1} (Jüttner et al., 2000; Wang and Chen, 2009; Renu, 2017). This method has used over a wide area as an application for removal of heavy metal from inorganic effluent (Larry D. Benefield and Morgan, 1999; EPA, 2000).

4.2.3. Ion exchange

Ion exchange defined as a chemical treatment process used to remove species of dissolved ionic form polluted aqueous streams. Remediation of both anionic and cationic pollutants can be affected via processes of ion–exchange. Insoluble ion exchangers are polyelectrolytes that have a high molecular weight are fixed ionic groups linked with a solid matrix. Ion exchangers, whether synthetic and natural, are applicable. There are vast different polymers that have been utilized as ion exchangers, but copolymers of divinylbenzene (DVB) and styrene are the most commonly used as synthetic organic ion–exchange resins. It can be used only for a metal solution at low concentration, and this process is extremely sensitive to the pH of the aqueous phase (James, 2001; Gunatilake, 2015).

Ion exchange resins can exchange specific ions inside the polymer with the ions from the solution that is passed during them. The same could be witnessed in natural systems like living cells and soil. "Ion exchangers are insoluble acids or bases, which have salts that are also insoluble; this enables them to exchange either positively or negatively charged ions" (Vemula, 2012). Attracting soluble ions by ion–exchange can be observed from the liquid phase to the solid phase, which is the most popular method used in industrial water treatment. As a cost–efficient process, the ion exchange method usually requires low–cost substances and convenient operations, and it is highly effective for the removal of heavy metals from aqueous solutions, special for the treatment of water with low heavy metals concentration (Dizge et al., 2009; Hamdaoui, 2009). The method has a few disadvantages in that there are materials that can spoil the resin; complexes breakage might occur as a function of the pH of the solution, settling time, and agitation time (Reichenberg, 1953).

4.2.4. Surface complexation models (SCMs)

An alternative to the approaches of experimental modeling are surface complexation models (SCMs) and have been applied in research to explain the biosorption of metals into biochar recently (Hayes, 1987; Alam et al., 2018) by weakly basic anion exchangers (Stöhr et al., 2001).

Although cation exchange may have played a role, the most important sorption mechanism was surface complexation through the interaction and bridging of metals (Jia et al., 2013). There are three surface complexation models: diffuse–layer model (DLM), constant capacitance model (CCM), and triple–layer model (TLM). The surface complexation model is relying on the idea of surface charge produced from amphoteric surface sites, which are able to react with anionic or cationic species from the liquid phase to form ion pairs at the surface, named surface complexes. It has been assumed that the adsorbent surface is a plane surface across which the functional groups are distributed uniformly. Surface charges are produced by the protonation or dissociation of surface groups. As a result, it can be supposed that protons are biosorbed directly on the surface (Jeon and Höll, 2004).

The surface complexation is formed by a reaction between functional surface groups and an ion in a surrounding solution, especially the inner–sphere surface of metal ion complexes (Bradl, 2004), which forms a stable unit (Schindler et al., 1976). The surface complexation model can describe the specific biosorption behavior (Schindler et al., 1976), very accurately at low cation concentrations, but has no ability to characterize biosorption curves obtained at high concentrations. For biosorption, the presence of functional surface groups is essential (Bradl, 2004).

Potentiometric titration is a method overwhelmingly used to determine both amounts and types of functional groups on the surface of the biosorbent (Yee et al., 2003).

High pH can cause carboxylic and hydroxyl groups to deprotonate (Chen et al., 2015) and therefore enhanced the surface complexation of heavy metals with functional groups (carboxyl and hydroxyl) (Lu et al., 2012).

Ho et al. (2017), the decrease of C=C group proved that the surface complexation of heavy metals had affected by delocalized π electrons, and (Jiang et al., 2012), revealed biosorption of Pb(II) with rice straw derived biochar by surface complexation with delocalized π electrons.

4.2.5. Electrostatic interactions

The electrostatic attraction has depended on the pH of the solution and point of zero charges (pzc) for biochar. When the pH of the solution is $< pH_{PZC}$ (pH of zero point charges), the biochar surface is charged positively, and electrostatic repulsion between functional groups and metal ions may occur (Mahdi et al., 2018). Presence of electrostatic attraction often led to increasing the kinetics of metal biosorption through the early first period of contact between the biosorbate and biosorbent (Jinsheng Sun et al., 2012).

4.3. Disadvantage of Traditional Methods in the Treatment

The progress of metallurgical and the use of different chemical materials and metals in a large number of industries have caused the production of large amounts of effluent liquid laden with heavy metals at high levels, many cases as bioavailable mobile and therefore species of toxic ionic heavy metals (Gadd, 1992; Calderon et al., 2003; Peakall and Burger, 2003). Because of their elementary non–degradable nature, heavy metals always pose an ecological threat seriously when discharged into the environment without regard to their chemical form (Kotrba, 2011).

The main mechanisms which have been used to diminish or remove the heavy metal ions, which are inside of effluents, are ion exchange, lime precipitation, adsorption into activated carbon, electrolytic methods, and membrane processes. All these techniques are generally high cost and have significant drawbacks, which include incomplete removal of metals, requirements for high–cost apparatus and monitoring systems, energy requirements or high reagent, or toxic sludge production or other waste generated that require disposal (Thirumavalavan et al., 2010).

The so–called biosorption, as an alternative. The main attractions of biosorption are:

- High selectivity
- High efficiency
- Cost–effectiveness
- Good removal performance
- Product recovery;

Raw materials that are whether abundant (seaweeds) or waste from other industrial processes such as (activated sludge process waste, fermentation waste) could be used as biosorbents that are often comparable to ion exchange resin efficiency (Volesky, 1999). Although both living and dead biomass can be used to biosorb hazardous organics, it is difficult to maintain viable biomass during biosorption as it needs supplies of nutrients continuously and preserve the microorganisms from organic toxicity (Aksu, 2005). Generally, biosorption is used for wastewater treatment to treat heavy metal pollutants

(Huang et al., 1990; Brady and Tobin, 1994; Nourbakhsh et al., 1994; Kapoor and Viraraghavan, 1995; Veglio and Beolchini, 1997; Say et al., 2001; Volesky, 2001). Biosorption can also be regarded as a promising tool for removing organic compounds from industrial waste streams and contaminated natural waters (Aksu, 2005).

5. BIOSORPTION

Biosorption is a physical, as well as a chemical process that takes place naturally in some biomass, allowing pollutants to passively accumulate and bind to their cellular structure (Volesky, 1990).

Biosorption was also defined by Volesky (2007), as the property of some biomolecules (or biomass types) for binding and concentrating selected molecules or other ions from aqueous solutions. Although heavy metal biosorption has become a common research subject motivated by the environment, it only represents one specific form of the concentration removal feature of the sorption mechanism.

Biosorption is a simple physico–chemical process that resembles a conventional ion exchange or adsorption. The difference relates to the nature of the sorbent, which, in this case, is of biological origin (Chojnacka, 2010a).

Biosorption and bioaccumulation distinguish in the place where the contaminants bound with cell. The first process is attached to the cell wall surface, and they also accumulate within a cell in the second process. Biosorption and bioaccumulation, either living (bioaccumulation) or non–living (biosorption), involves interactions and concentration of toxic metals and organic contaminants (e.g. dyes). The main usage of biosorption and bioaccumulation was the removal of metal cations from the solutions. According to the literature, the biomass–metal interactions dates back to the 1960s (Chojnacka, 2010a). Table 5.1 shows the comparison between the biosorption and bioaccumulation process.

Table 5.1. The comparison between biosorption and bioaccumulation process (Chojnacka, 2010b)

Biosorption	Bioaccumulation
Passive process	Active process

Table 5.1. The comparison between biosorption and bioaccumulation process (continued)

Metals are bound with cellular surface	Metals are bound with cellular surface and interior
Adsorption	Absorption
Reversible process	Partially reversible process
Biomass is not alive	Biomass is alive
Nutrients are not required	Nutrients are required
Single–stage process	Double–stage process
The rate is quick	The rate is slow
Not controlled by metabolism	Controlled by metabolism
No danger of toxic effect	Danger of toxic effects caused by contaminants
No cellular growth	Cellular growth occurs
Intermediate equilibrium concentration of metal ions	Very low equilibrium concentration of metal ions

The method of biosorption includes a liquid phase (solvent, typically water) and a solid phase (biosorbent or sorbent, biological material) comprising a dissolved species to sorb (metal ions, sorbate). Since existing a high affinity from the biosorbent to the biosorbate material, the latter is attached and attracted by various mechanisms. The procedure continued until the equilibrium between the solid–bound sorbate species amount, and the portion remained in the solution is established (Dhara Shukla and Vankar, 2015).

Metals are considered materials of commodities. Large quantities of various metals types are needed to support our life of style. Its production and common usage is the cause of why the amounts of metals present in the environment increase. By human technological activities, metals become 'mobilized' from natural precipitate as their sources and continue to hit un–predictable amounts into natural cycles. A long way from being inert, they are persistent, posing a relatively recent recognition and recognition of the significant danger to balance of nature and eventually to human safety. Biosorption occurs as an attractive and economical method due to the use of either natural, sustainable, or even biomaterials waste, especially for inexpensively removing metals from industrial solutions and effluents where they are present even at low concentrations (Naja and Volesky, 2011).

Much attention has been paid over recent years to use biotechnology throughout controlling and eliminating contaminations of metal, and because of its possible use, it progressively has become a hot subject in the area of control of metal pollution. So biosorption is an alternate method that includes a range of sorption sources, including yeast, bacteria, algae, fungi, leaves, plant, etc. (Jinsheng Sun et al., 2012).

5.1. Biochars as Biosorbent for Removing of Heavy Metals in Aqueous Media

Biochars research shows that biochar can efficiently biosorb heavy metals in aqueous media and wastewater from plants and animal residues (Higashikawa et al., 2016; Inyang et al., 2016; Tan et al., 2016; Dai et al., 2017; Zhou et al., 2017).

Many types of research have shown that biochar can remove pollutants from water and wastewater, either organic or inorganic pollutants, through biosorption (Ahmed et al., 2016). Also, shown that sludge–derived biochar was cost–effective and reusable biosorbent for the removal of the antibacterial drug (Chowdhury et al., 2019). Table 5.2 presented the removal of heavy metals by different biochar via biosorption from water and wastewater.

Table 5.2. Removal of heavy metals from water and wastewater by selected biochar

Heavy metals	**Initial concentration (mg L^{-1})**	**Feedstock**	**Pyrolysis temperature**	**Applied dose (g L^{-1})**	**Removal efficiency (%)**	**References**
Cd(II)	20	Rape straw	600	1.25	100	(Li et al., 2017)
Cr(VI)	200	Peanut hull	450–650	2	10–70	(Han et al., 2016)

Table 5.2. Removal of heavy metals from water and wastewater by selected biochar (continued)

Pb(II)	150	Sawdust and swine manure	400	0.4	100	(Liang et al., 2017)
Cu(II)	0.5	Silver birch	450	140	~25	(Komkiene and Baltrenaite, 2016)
Zn(II)	0.4	Scots pine			~20	

The removal of heavy metal ions by different biochar was listed in Table 5.2. The removal of heavy metals by biochar depended on the feedstocks and types of heavy metals.

5.2. Biochar Characteristics for Metals Removal

Biochar is characterized as the porous carbonaceous solid obtained through the thermochemical conversion of biomass material without oxygen atmosphere (pyrolysis) (Lehmann and Joseph, 2015). As shown by Verheijen et al. (2010), biochar surface area and porous structure may differ considerably based on feedstock and processing conditions, such as temperature of pyrolysis or heating period. In general, the biochar surface area increases with the temperature of pyrolysis (Chun et al., 2004; Ahmad et al., 2012; Lü et al., 2012; Jindo et al., 2014).

Biochar's ability to remove metals is influenced by various physical and chemical characteristics, including pH, surface area, fixed carbon, electronegative surface charge, and functional surface groups. Biochar characterization was compared with the results of biosorption and modeling to evaluate biochar metal removal mechanisms (Burch, 2018).

Biosorption of cationic metals increases with pH, so alkaline biochar pH can affect solution pH and subsequent removal of metals. The biochar surface area is important because it has been shown that high surface area increases the ability of the biochar at biosorption (Chen et al., 2011).

5.3. Production and Properties of Biochar

There is a large amount of common waste in the world, such as agricultural waste and sludge. An option for environmental sustainability could be the conversion of common waste to biochar. These wastes include sludge waste, manure, biomass crops, and agricultural residues can generally be used as feedstock for biochar synthesis. Different feedstocks have different element composition proportions and therefore have different properties, so the biochar prepared from different feedstocks has different performance (Wang and Wang, 2019).

The use of waste biomass for biochar production is a reasonable and beneficial option in terms of maintaining an eco–friendly environment because there is no economic value for these types of feedstocks, and they do not compete with food crops for land requirements (Kambo and Dutta, 2015).

5.3.1. *C. annuum* seeds as feedstock

Pepper, particularly *Capsicum annuum*, is a general name for plants that come from the Capsicum species of Solanaceae family, whose products have been used as spices and vegetables (Luning et al., 1995). It is eaten as a cooked and raw vegetable and is also widely used to make paste, pickle, and sauce. Red ground pepper produced by drying and grinding red pepper is used in the food industry as a spice and flavoring ingredient (Isidoro et al., 1995). Moreover, (Bosland, 1994) reported its wide variety of medical applications, from increasing appetite, relieving arthritis–related pain, to the diuretic effect.

Red pepper is cultivated in some regions in Turkey like Kahramanmaraş, Gaziantep, and Şanlıurfa cities of Turkey are well known for its good tastes and flavors. Red pepper (*C. annuum*) is a quite popular and commonly used Turkish pepper spice. It can be used for various purposes such as seasoning, flavoring, aroma–providing, coloring, or as a pungent good (Arslan and Özcan, 2011; Omolo et al., 2014; Korkutata and Kavaz, 2015). The major plantation area of red pepper in Turkey is Maraş and Urfa (Poyrazoğlu et al., 2005). The most important city in connection to the red pepper plant in Turkey is Kahramanmaraş city Figure 5.1 (Mustafa, 2018).

Figure 5.1. Kahramanmaraş red pepper

China is the number one producer of this pepper, which produces 12,531,000 tons/year followed by Turkey, which produces 1,745,000 tons/year (Omolo et al., 2014). Red pepper for spice, particularly in the south and southeast cities of Turkey, is of the primary revenue source for farmers (Tursun et al., 2012).

C. annuum seeds, which are cheap, abundant, and easily accessible residue, are one of the agricultural by–products from the waste of pepper paste manufacturing plant. After eating or processing the flesh, its seeds are separated from the pods and discarded as waste (El-Adawy and Taha, 2001). CASB was prepared from these seeds and used in the treatment of contaminated solution.

5.3.2. Biochar production processes

BC can be produced from various types of biomass, particularly low–cost wood biomass, agricultural biomass, solid waste, and animal litter, through many thermochemical processes: pyrolysis (fast and slow), torrefaction, gasification, and hydrothermal carbonization (Meyer et al., 2011; Qian and Chen, 2013; Xu et al., 2013). The most popular thermochemical process for biochar production is pyrolysis, at which the organic components are broken down without oxygen atmosphere at an adjustable temperature. The key parameters influencing pyrolysis products are heating rate, holding time, reaction temperature, and types of feedstock (Zhang et al., 2019b).

5.3.2.1. Pyrolysis

Without oxygen and at a temperature between 300 to 900°C, pyrolysis is an effective method for converting biomaterial into high–value materials such as BC, bio–oil, and syngas (Gell et al., 2011; Heidari et al., 2014; Liu et al., 2014; Jeong et al., 2015; Lee et al., 2016; Shafaghat et al., 2016).

The pyrolysis may generally be divided into slow pyrolysis (long residence time and low heating rate) and fast pyrolysis (short residence time and high heating rate) depending on heating rate, temperature, pressure and residence time (Lima et al., 2010; Mohan et al., 2014; Russell et al., 2017). Toxic substances emitted through the pyrolysis process are few if compared to gasification and combustion processes (Agarwal et al., 2015).

Slow pyrolysis is performed at a low heating rate (less than 10°C min^{-1}) and takes a few minutes to many hours (short residence period) that is widely used to facilitate biochar production. Generally, the biochar that is produced at a lower pyrolysis temperature (< 500°C) has attractive features for the treatment of inorganic pollutants (Oliveira et al., 2017). Fast pyrolysis occurs at a higher heating rate (~1000°C S^{-1}) for the production of the main product, which bio–oils (as 70%) and biochar (Mohan et al., 2014). Relatively high yield from slow biochar pyrolysis (35%) if compared to fast pyrolysis (10%) and gasification (10%) (Sohi et al., 2009; Mohan et al., 2014).

However, there are other technologies for pyrolysis (e.g., torrefaction and microwave–assisted pyrolysis), which can be applied to convert municipal solid waste to biochar thermochemically (Mohan et al., 2014).

Torrefaction is indeed a process of pyrolysis which is performed at low temperatures (200 to 280°C) to assist decomposition of biomaterials partly (Viraj Gunarathne, 2017).

Microwave–assisted pyrolysis is a new technique of pyrolysis. When comparing its performance with conventional pyrolysis processes, can be served as an environmentally friendly and economically in the biochar preparation process (Luque et al., 2012; Yu et al., 2017).

5.3.2.2. Gasification

Gasification defines a thermochemical process that primarily decomposes a carbon source to a gassy mixture (syngas including CH_4, CO_2, CO, H_2, and limited amounts of hydrocarbons) by providing a controlled quantity of oxidizing agent at high temperatures (> 700°C) (Qian et al., 2015; Wang et al., 2016; Zhang et al., 2017a). The typical yield of biochar via the gasification process is about 10 wt% of the biomaterial. Generally, because of the conversion of carbon to carbon monoxide (CO) in the existence of an oxidizing agent (steam or O_2), the biochar prepared through the gasification process would be less than pyrolysis (Mohan et al., 2014). It should be noted that biochar produced through the gasification process includes high quantities of alkali and alkaline earth metals (Mg, Si, K, Ca, etc.) and highly toxic compounds of polycyclic aromatic hydrocarbons (PAHs) (Kloss et al., 2012; Kambo and Dutta, 2015). The existence of PAHs during pyrolysis was also investigated regarding the development of smoke (Mara dos Santos Barbosa et al., 2006).

5.3.2.3. Hydrothermal Carbonization

Hydrothermal carbonization (HTC), distinct from processes of gasification and pyrolysis that commonly are applied for low moisture biomaterial, is more suited for high moisture content biomass applications (Wilk and Magdziarz, 2017; Lee et al., 2018). Biomass hydrothermal carbonization is indeed a cost–effective path to biochar production because it is usually performed under pressure in the water at low temperatures of 180 to 250°C (Libra et al., 2011).

5.4. Environmental Factors Affecting Biosorption of Contaminants on BC

Batch studies typically focus on studying factors that influence biosorption, which is critical in determining the maximum capacity for biosorption of any biomaterial. Many researchers found that certain biosorption factors include biochar properties, de–mineralizing and deashing treatment, ions co–existed, functional groups, pH, temperature, initial soluble matter concentration, a dosage of biosorbent and its size, ionic strength, and agitation speed.

Here we described the factors mentioned above, which influenced the removal of the contaminants in the aqueous systems in Figure 5.2.

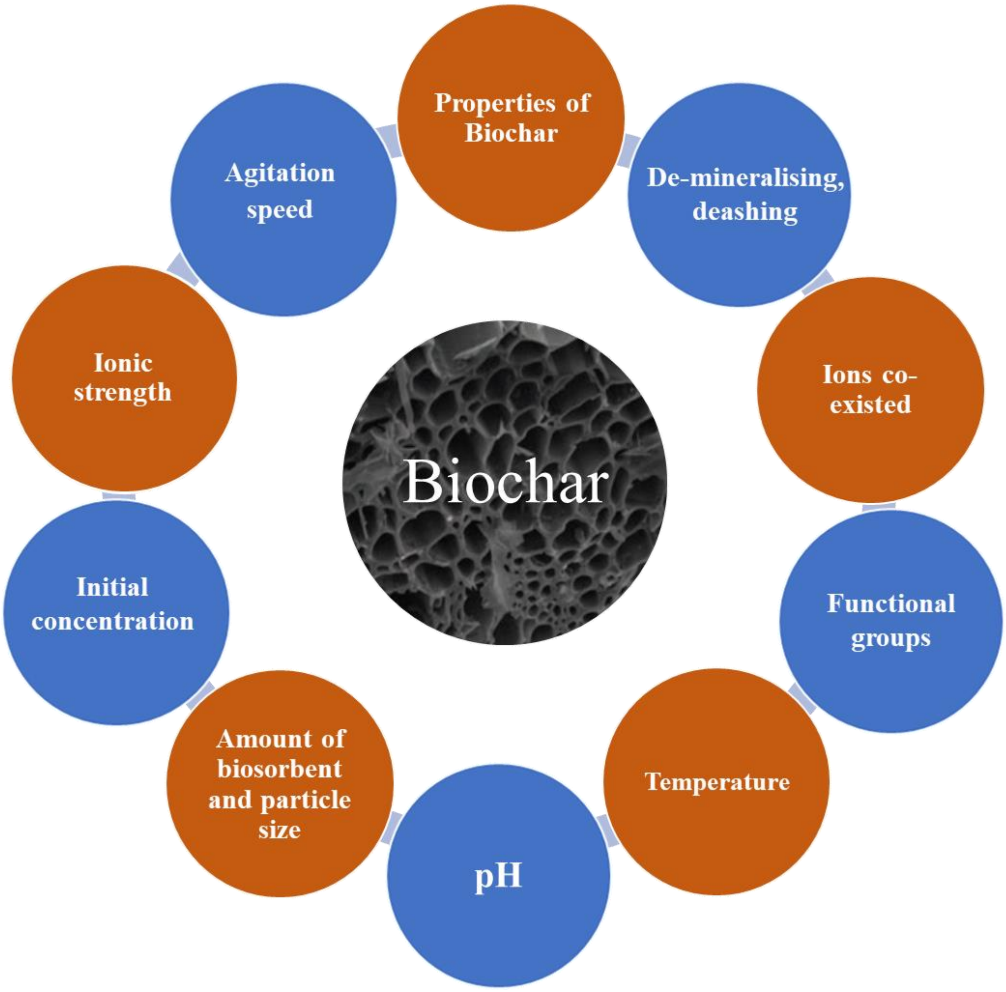

Figure 5.2. Environmental factors affecting the biosorption of contaminants onto BC

By altering the removal processes involved in the remediation of specific contaminants in aqueous environments and soil, these factors have a significant impact on the overall biosorption capacity of BC (Abbas et al., 2018).

5.4.1. Effect of BC properties

The temperature of pyrolysis, feedstock, time of residency, and thermochemical conversion technique has significant impacts on biochar properties. It is also clear that the factors that were mentioned above can get a noticeable impact on the effectiveness of biosorption towards different pollutants. Temperature presumably is a key parameter from these influences (Tan et al., 2015). The temperature of a pyrolytic was observed to have more impact on the biochar's structural characteristics and isotherm shape than the feedstocks for biomass (Chen et al., 2012c).

Chen et al. (2012b); Kim et al. (2013), reported that the temperature of a pyrolysis process of biomass influenced the biosorption rate of the compounds via biochar for the reason that the temperature influenced the degree of carbonization and the surface functional groups of biochars. The biomass organic matter was fully carbonized at higher temperatures, the surface area was significantly increased, and more nanopores were existed, resulting in a sharp improvement in the biosorption rate of pollutant such as Naphthalene (NAP).

In particular, the pyrolytic temperature was also observed to have effects on heavy metal biosorption. Kim et al. (2013), noticed that the temperature of pyrolytic had a greatly affected on biochar properties such as (elemental, structural, and morphological properties).

The biosorption potential of biochar was also strongly affected by feedstock's natural compositions. The biosorption capacity for different types of biochar for pollutants were differed at the same pyrolysis conditions (Sun et al., 2014). Liu et al. (2010), reported that the surface of biochar produced via hydrothermal treatment has more groups that contain oxygen than the process of pyrolysis, which affects the efficiency of biosorption.

5.4.2. Effect of de-mineralizing and deashing

The understanding of the impact of de–mineralization and deashing treatment on their biosorption of water contaminants by biochar is limited. It is observed that these methods could have a considerable effect on biochar's biosorption properties. That was, in particular, because deashing can have a significant impact on the surface properties and composition of the biochar. However, the influence of treatment with de–mineralization and deashing is currently unclear. There is very little experimental evidence of such influence that needs further investigations (Tan et al., 2015).

5.4.3. Effect of ions co-existed

The ions co–existence exerts a significant effect on the equilibrium biosorption capacity, particularly when applying biochar in the actual water system, due to complex contaminants generally co–exist in the environment and interactively effects the efficiency of biosorption. The biosorption studies of co–existed ions can help to better understand the mechanism of pollutant biosorption by biochar in the natural (Tan et al., 2015).

5.4.4. Effect of the functional groups of biosorbent surface

Biosorption capacity is significantly affected by functional groups. FTIR has been used to detect effectively functional groups scattered in the biosorbents and also to investigate the vibration frequency variations of those groups (Kamarudzaman et al., 2015).

BC has a large surface area, small pore sizes in the skeleton of carbon, rich in various functional groups. Biochar has a well–developed porous structure and is rich in minerals and functional groups containing oxygen (Weber and Quicker, 2018). Because of the different types of biochar, there are different surface–active and functional groups, which lead to different organic pollutant biosorption mechanisms by different biochars (Dai et al., 2019). The surface of biochar may have numerous functional groups, including hydroxyl, ketone, carboxyl groups, phenolic, nitro, amino, aldehyde, and ester (Kambo and Dutta, 2015). The functional groups (–COOH, R–OH, and –OH) are active functional groups to govern in the removal of pollutants by interacting with each other (Oliveira et al., 2017).

5.4.5. Effect of solution pH

The pH of the aqueous solution typically plays a significant role in the process of biosorption and affects not only the dissociation sites but also the solution chemistry of dyes and heavy metals as well as the activities of the functional groups of biomaterial. Also, the pH significantly influences the availability of metal ions for biosorption in metals (Yang and Volesky, 1999; Esposito et al., 2002). The solution pH is a significant parameter for control that affects the biosorption process since it determines the biosorbent's surface charge, the ionization degree, and the biosorbate species (Dhanarani et al., 2016; Yu et al., 2016). A competition between H^+ ions and metal ions is created at high concentrations of H^+ (Du et al., 2005; Zhang et al., 2010; Du et al., 2016; Zhang et al., 2016b). Hydroxyl groups convert to O^- ions by raising the biosorbent's total negative charge, and biosorption of Pb(II) is significantly enhanced (Zhou et al., 2015a; Zhou et al., 2015b). A further reason which enhanced the efficiency of biosorption with increased pH is a reduction in metal ion solubility at high pH.

Biochar has different surface functional groups (especially groups including oxygen, such as hydroxyl, –OH; and carboxylate, –COOH). With the increased pH of the solution, the behaviour of those functional groups was changed. At low pH, almost all of those functional groups that exist on biochars are protonated and offered in form positive charge. Moreover, the existence of large numbers of H^+ and H_3O^+ in the aqueous media could be competing with the cation available on biochars for biosorption sites. Thus there would be electrostatic repulsion between the positively charged biochar surface and cation pollutants. Therefore a lower biosorption was found in most experiments at low pH (Tan et al., 2015). The competition between protons and metal ions for binding sites has been reduced by increasing the pH value, and more binding sites have been released because functional groups have been deprotonated (Lu et al., 2012). The above trends were observed during the biosorption process of various heavy metals onto different biochars. Concerning the metals cations, the biosorption capacity increased with an increasing pH in most studies. Considerably, the pH of the solution influenced the speciation of metal, and therefore, affected the biosorption of the heavy metal onto biochar.

5.4.6. Effect of temperature

The majority biosorption of adsorptive contaminants is endothermic. Therefore the higher temperature generally improves the biosorption removal of the biosorbate by raising its kinetic energy and surface activity (Vijayaraghavan and Yun, 2008). Higher temperatures, however, can also reflect negatively through physically damaging to the biosorbent; therefore, room temperature is generally desired for processes of biosorption (Park et al., 2010). Previously, most studies have indicated that the biosorption of pollutants via biochars seemed to be an endothermic process and that the biosorption capacity was raised with an increase in temperature (Liu and Zhang, 2009; Chen et al., 2011; Zhang et al., 2013). Liu and Zhang (2009), stated that the biosorption of lead ions on BC derived from rice husk and pinewood preferred high temperature.

5.4.7. Effect of initial concentration of heavy metals

The initial concentrations of metal ions have a significant influence on the biosorption capacity of different biosorbents (Michalak et al., 2013). This discovery can be clarified by the assumption that the initial concentration works as a driving force in overcoming resistance to the mass transfer of metal ions between both the surface of the biosorbent and the solution (Arief et al., 2008).

5.4.8. Effect of amount of biosorbent and particle size

Biosorbent dose has a strong influence on biosorption and determines the potential of biosorbent via the number of binding sites accessible for removal of metal ions at specified initial concentrations (Yuvaraja et al., 2014). With the increasing dosage of biosorbents, more surface area for biosorption is obtainable, and that is the result of increasing active sites on the biosorbent, facilitating the penetration of metal ions into biosorption sites (Azouaou et al., 2010). Heavy metal ions were biosorbed more quickly by the biomass, whose particle size is small, and the equilibrium was reached faster than that achieved by the large particle size biomass. That was most likely because the total surface area was increased, and more sites were available for the uptake of metal ions (Nadeem et al., 2008).

Chen et al. (2011), showed a decrease in biosorption capacities by increasing the BC concentration. At the same time, an increase in the concentration of the biosorbent led to an increase in the biosorption efficiency of the whole heavy metals, as all active sites were increased. Similar findings by (Tsai and Chen, 2013) have been reported. Those who reported that the number of biosorption sites was increased as biosorbent doses were increased.

5.4.9. Effect of ionic strength

The capacity of biosorption decreases with increasing ionic intensity, as metal ions and other ions in the environment compete to attach with functional groups on the biomass. For instance, sodium in many wastewaters is generally concentrated and has a reduced effect on the biosorption of heavy metal ions (Liu and Wang, 2009).

5.4.10. Effect of agitation speed

Agitation speeds have been observed to have a positive influence on the non–agitated system. In the first 30 minutes of biosorption, an increase of biosorption was noted for the agitated samples. That was because agitation facilitates good contact between the binding sites for biomass and the metal ions in solution and thus promotes the efficient transfer of biosorbate ions to the biosorbent sites (Bai R and Abraham, 2001).

5.5. Equilibrium Isotherms and Kinetic Studies on Biosorption

Equilibrium biosorption isotherm is of fundamental importance in biosorption system design. Equilibrium experiments in biosorption give the biosorbent capacity. Equilibrium relationships between biosorbent and biosorbate are explained by biosorption isotherm, generally the ratio between the quantity biosorbed and the remaining in the solution at equilibrium and a constant temperature (Han et al., 2005).

During the biosorption process, various forms of biosorption isotherms have expressed the relationship between the equilibrium heavy metals concentration in the liquid phase and the quantity of heavy metal removal at pH and steady temperature (Esmaeili and Beni, 2014).

By certain constant values, the biosorption isotherm is an index on the properties of the biosorbent surface, the affinity of the biosorbent, and gives comparability in biosorption capacity of the biomaterial for different heavy metals (Han et al., 2005; Abu Hasan et al., 2016).

In most published studies on biosorption, researchers used Freundlich and Langmuir isotherm models since these models are better adapted to estimate the data about experimental equilibria of biosorption (Gomez-Gonzalez et al., 2016).

5.5.1. Biosorption isotherm modeling

A biosorption isotherm is a graphical description that indicates the relation between the amount biosorbed by a unit weight of biosorbent (e.g., activated carbon) and the amount of biosorbate remained at equilibrium in a test medium. It describes the distribution of biosorbable solute between the solid and liquid phases at different concentrations of equilibrium (Rouquerol et al., 2014).

5.5.1.1. Langmuir isotherm model

Here quantitatively explains the forming of a monolayer biosorbate on the external surface of the biosorbent and no additional biosorption afterward. The Langmuir described the mass balance of solutes between solid biosorbent and liquid biosorbate phases (Chung et al., 2015). The Langmuir biosorption isotherm is the more extensively applied model in biosorption of contaminants from aqueous solutions and dependent on the following considerations: (1) The biosorption is a monolayer. (2) Biosorption occurs at specified homogenous locations on the biosorbent. (3) When the contaminant takes a site, no additional biosorption can occur at this site. (4) The energy of the biosorption is constant and need not rely on the degree of occupancy of active sites of a biosorbent. (5) It is assumed that the strength of the intermolecular force of attraction falls quickly with distance. (6) Biosorbent has a limited capacity for the removal of contaminations. (7) Whole the sites on biosorbent are equivalent and identical in terms of the energy. (8) The biosorbent is homogenous in structure. (9) Neighbouring sites do not interact with biosorbed molecules (Langmuir, 1916). Based on those assumptions, the following non–linear (Equation 5.1) was formed by Langmuir:

$$q_\mathrm{e} = \left(\frac{q_\mathrm{m} \cdot K_\mathrm{L} \cdot C_\mathrm{e}}{1 + K_\mathrm{L} \cdot C_\mathrm{e}} \right) \tag{5.1}$$

Where q_m (mol g^{-1}) is the maximum capacity for biosorption, q_e (mol g^{-1}) is biosorption capacity of the biosorbent at equilibrium, C_e (mol L^{-1}) is the metal concentration at equilibrium in solution, and K_L (L g^{-1}) is a Langmuir constant, which describes affinity between both the metal ion and biosorbent and relates to the free biosorption energy. It can be used to evaluate the biosorbent's suitability for the biosorbate by using the R_L, dimensionless constant (Hall separation factor) as follows (Equation 5.2):

$$R_\mathrm{L} = \frac{1}{1 + K_\mathrm{L} \,.\, C_\mathrm{o}} \tag{5.2}$$

Where C_o (mol L^{-1}) is the initial metal concentration, the R_L parameter indicated the isotherm type. It means unfavourable if the $R_\mathrm{L} > 1$, means linear if $R_\mathrm{L} = 1$, means favourable if $0 < R_\mathrm{L} < 1$, and means irreversible $R_\mathrm{L} = 0$ (Hall et al., 1966).

5.5.1.2. Freundlich isotherm model

Freundlich's isothermic equilibrium model has an empiric equation used to describe multilayer biosorption with the interaction between biosorbed molecules (Rangabhashiyam et al., 2014). It is a non–linear form given as follows (Equation 5.3):

$$q_\mathrm{e} = K_\mathrm{F} \cdot C_\mathrm{e}^{1/n} \tag{5.3}$$

Where K_F (L g^{-1}) is a Freundlich linearity coefficient and related to the biosorption capacity, and n (heterogeneity factor) is a Freundlich constant indicative of the intensity of the biosorption.

This model applies to the biosorption by a uniform energy distribution and reversible biosorption on heterogeneous surfaces. The Freundlich equation assumes that at the endpoint of biosorption centers of a biosorbent, the biosorption energy reduces exponentially (Freundlich, 1906). The constants of Freundlich are empiric constants that can be dependent on many environmental factors. The magnitude of the exponent *n* is indicative of the favourability and capacity of the biosorbent/biosorbate system. It is generally stated (Helby, 1952) that values of *n* in the range:
2 to 10 represent good,
1 to 2 moderately difficult,
less than 1 poor biosorption characteristics.

5.5.1.3. Dubinin-Radushkevich (D-R) isotherm model

Isotherm model of Dubinin–Radushkevich could be employed to calculate the apparent free energy and biosorption characteristics (Radushkevich, 1949; Dubinin, 1960; Dubinin, 1965). Tounsadi et al. (2015), the isothermal model of Dubinin–Radushkevich is more general than that of the Langmuir model. The D–R isotherm is represented through the following (Equation 5.4) (Dubinin and Radushkevich, 1947):

$$q_e = q_m \cdot \exp(-\beta \cdot \varepsilon^2) \qquad (5.4)$$

Where q_e (mol g^{-1}), is the amount of metal ion biosorbed per unit mass of the biosorbent; q_m (mol g^{-1}) is the maximum value of biosorption of the metal ions; and β (mol J^{-1})^2, is the activity coefficient, which depends on the biosorbent's free energy. The parameter ε (kJ mol^{-1}) is the Polanyi potential and is estimated by (Equation 5.5) (Esmaeili and Beni, 2014):

$$\varepsilon = RT\ ln(1 + \frac{1}{C_e}) \qquad (5.5)$$

Where R (8.314 J mol^{-1} K^{-1}) is the total constant of gas, and T in Kelvin, absolute temperature of solution.

At last, according to the (Equation 5.6), the mean biosorption free energy (E; kJ mol^{-1}), in the D–R model, was calculated:

$$E = \left[\frac{1}{\sqrt{2\beta_{\mathrm{DR}}}}\right] \tag{5.6}$$

If the mean biosorption free energy (E; kJ mol^{-1}) is in the range from 8 to 16, the biosorption process follows the chemical ion–exchange process, and if it is less than 8, the physical biosorption prevailing (Hobson, 1969).

5.5.2. Biosorption kinetic modeling

In the biosorption study, the kinetic studies are very necessary and predict the biosorbate removal rate, which offers important knowledge for the design of full–scale batch and fixed–bed biosorption processes and biosorption efficiency. The biosorption mechanism depends on both the physical and chemical characteristics of the biosorbent and the process of mass transfer (Kumar et al., 2014; Vijayaraghavan et al., 2017).

Possibly the most significant factor in the biosorption systems design being the residence time and the dimensions of the reactor controlled by the system kinetics is the kinetic characterization of metal biosorption (Pagnanelli, 2011).

While the range of biosorption completely depends on the initial and final state of equilibrium, the rate of biosorption depends on the path from the initial to the final stage. To properly understand the biosorption kinetics, for each step that occurs during the process, an accurate rate equation must be obtained. Simple mathematical terms, such as pseudo–first and pseudo–second–order equations, based on biosorption at unfilled biosorbent surface sites, can only be used if they may correctly explain the full kinetic experiences (Lodeiro et al., 2006).

To understand the biosorption kinetics of heavy metals and quantify the amount of removal in biosorption kinetics, the pseudo–first and second–kinetic models (in the parallel) were commonly used, and one is often found to be better than the other according to the peripheral difference in the correlation coefficient (Liu and Liu, 2008; Febrianto et al., 2009).

To explain the mechanism of biosorption kinetics of heavy metals onto BC in aqueous media, three models (pseudo–first, pseudo–secondary, and intra–particle diffusion models) were employed.

5.5.2.1. Lagergren pseudo-first-order kinetic model

By Lagergren (1898), the pseudo–first–order model proposed. This model is given as follows (Equation 5.7):

$$q_{\mathrm{t}} = q_{\mathrm{e}}(1 - e^{-k_1 . t}) \tag{5.7}$$

In these equations, q_t and q_e (mg g^{-1}) are the capacity of biosorption at time t (min) and at equilibrium time, respectively. k_1 parameter (min^{-1}) is the pseudo–first–order model constant.

Several researchers have mentioned that the pseudo–first–order kinetic model is not appropriate for predicting the kinetics of biosorption for the entire process of biosorption, and it commonly suits well over the initial period of rapid biosorption (Belala et al., 2011; Vijayaraghavan, 2016). The occupancy rate of biosorption sites proportional to the number of vacant sites has been taken into account in this model (Hossain et al., 2015; Tounsadi et al., 2015).

5.5.2.2. Pseudo-second-order kinetic model

The pseudo–second–order kinetic model Ho and McKay (1999), is designed on the principle of equilibrium capacity of biosorption. Whereas, the equilibrium capacity for biosorption is proportionate to the number of active sites filled on the biosorbent and follows the process of chemisorption (Ho and McKay, 2003).

This model can be represented as the (Equation 5.8):

$$q_\mathrm{t}=\left(\frac{k_2 \cdot q_\mathrm{e}^2 \cdot t}{1+k_2 \cdot q_\mathrm{e}^2 \cdot t}\right) \tag{5.8}$$

Where k_2 (g mg^{-1} min^{-1}): is the rate constant of the pseudo–second–order.

5.5.2.3. Intraparticle diffusion model (IPD)

The intraparticle diffusion model by Weber and Morris is built on the hypothesis that one of the following or by a combination of steps which including external or film diffusion, surface diffusion, pore diffusion, and biosorption on the biosorbent pore surface can be used to control the biosorption process (Weber and Morris, 1963; Fierro et al., 2008). The model is given as the following (Equation 5.9):

$$q_\mathrm{t} = K_\mathrm{p}\left(t^{1/2}\right) + C \tag{5.9}$$

In this equation, q_t (mg g^{-1}) is amount of heavy metals biosorbed at time t, C is the constant affined to the thickness of the boundary layer, and K_p (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion rate constant that is calculated by the extrapolation of the linear portion of the plot of q_t versus square root of time $t^{1/2}$.

6. MATERIALS AND METHODS

6.1. Glassware

Glassware such as beakers, volumetric flasks, conical flasks, pipettes, burettes, used for experiments was first cleaned with a detergent. They were thoroughly rinsed several times in tap water and finally in distilled water.

6.2. Chemicals and Reagents Used

The following chemicals have been used for the present studies: $Pb(NO_3)_2$ was purchased from (analytical grade, Merck). The chemicals used in the present study were of analytical grade. The stock solutions at a concentration of 1000 mg L^{-1} of Pb(II) was prepared with ultrapure water.

6.3. Instruments-Equipment

The following instruments–equipment were used in the present study: Atomic Absorption Spectrophotometer (Perkin Elmer, Analyst 400), Thermo Magnetic stirrer Variomag and Cimarec i Poly 15 Multipoint, pH meter (WTW−Inolab 720), Peristaltic pump (Ismatec IP 8), Tube furnace (Protherm Furnaces), Centrifuge (MPW 350R), Zeta sizer (Malvern Zetasizer nano ZS), SEM (Hitachi Regulus 8230 FE−SEM), and EDX.

6.4. Preparation of CASB

Fresh *C. annuum* L. samples were purchased from local supermarkets (Adana, Turkey). After the pods were opened, the CASs were extracted, washed by pure water repeatedly, followed by drying at 80°C in an oven, and crushed. Finally, dried biosorbent was sieved to take particle size as <300µm by using ASTM standard sieve and used as feedstock.

These samples of the feedstock were used for biochar production, then were placed in ceramic crucibles as given as in Figure 6.1.

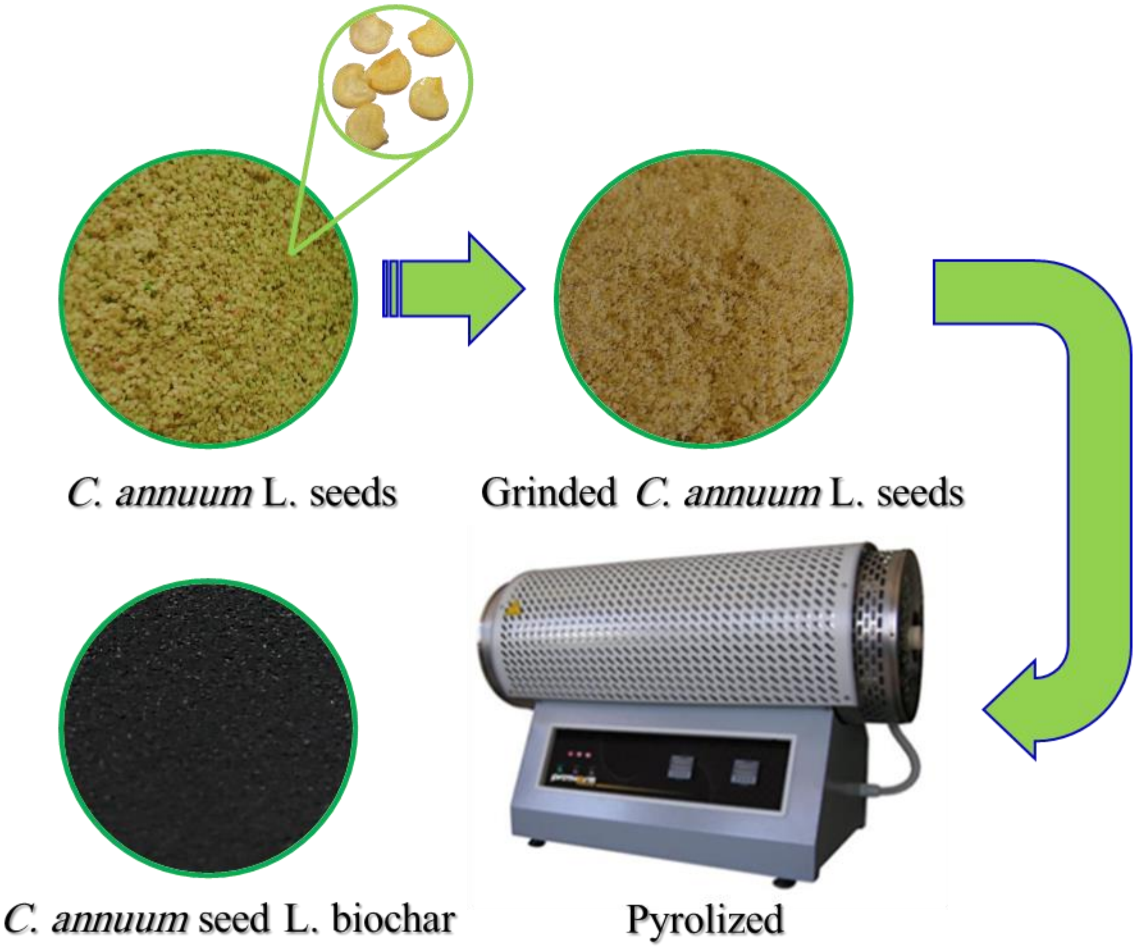

Figure 6.1. Photographs for the preparation of CASB

Finally, they were pyrolyzed in the tube furnace at the oxygen–free atmosphere at 400°C of pyrolysis temperature at about 85 min. Then, the biochar samples were left to cool at room temperature (Pan et al., 2013) and stored in sealed glass bottles before use.

6.5. Preparation of Metal Solutions

A stock solution of Pb(II) (1000 mg L^{-1}) has been prepared by dissolving an exact amount (1.5985 g) of $Pb(NO_3)_2$ (analytical grade, Merck) in ultrapure water. The stock solution is diluted to prepare other concentrations ranged from 25 to 400 mg L^{-1}. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted with 0.1 M NaOH or 0.1 M HCl to the desired values.

6.6. Batch Biosorption Studies on Removal of Pb(II) by CASB

The biosorption capacity of the biochar was optimized by varying physical parameters, and the analysis were carried out using Atomic Absorption Spectrophotometer (AAS). Batch biosorption experiments were performed by changing the operating parameters like solution pH, biosorbent dosage, contact time, and initial concentration of the metal ions. The results are based on the uptake of Pb(II) from the aqueous media.

In each batch experimental study (excluding biosorbent dosage) accurately weighed quantity (0.050 g) of CASB was added to 25 mL of Pb(II) solutions (100 mg L^{-1}) in beakers and the system was agitated at a constant stirring rate of 250 rpm on the multipoint magnetic stirrer. The experiments were replicated thrice, and the presented results were their average values. The biosorption capacity (q_e) of CASB was calculated from the following general mass–balance (Equation 6.1):

$$q_e = \frac{V(C_i - C_e)}{m} \qquad (6.1)$$

Where q_e (mg g^{-1}) is the biosorption capacity, C_i and C_e (mg L^{-1}) are the initial and the equilibrium concentrations of Pb(II) in the aqueous phase, respectively. m (g) is the weight of CASB, and V (L) is the volume of solution.

6.6.1. Effect of Different Parameters Influencing Biosorption

6.6.1.1. Effect of pH

Batch experiments have been carried out in pH 1, 2, 3, 4, 5, and 5.5 for Pb(II), keeping other parameters constant. The most suitable pH for biosorption was determined. Initially, adjusting the pH to the desired values by the addition of little drops of NaOH or HNO_3 at a concentration of 0.1 M, then mixing the biosorbent with 25 ml of 100 mg L^{-1} Pb(II) ion for 60 minutes.

6.6.1.2. Effect of biosorbent dose

Solutions containing 100 mg L^{-1} Pb(II) ion were treated with biosorbent doses from 0.4 to 6.4 g L^{-1} solution for 60 minutes, and the most appropriate amount of biosorbent was determined.

6.6.1.3. Effect of contact time

The contact time for batch experiments has been varied from 5 minutes to the point where there is no change in the amount biosorbed with an increase of contact time. The range used is from 5–90 minutes at 25 ± 1°C.

6.6.1.4. Effect of initial metal ion concentration

Investigation of the impact of the initial metal ion concentration on biosorption, solutions containing 25–400 mg L^{-1} Pb(II) ion were used for the BC at the optimum conditions determined.

6.6.1.5. Effect of temperature

Investigation of temperature effect on metal biosorption; 2.0 g L^{-1} biosorbent sample was treated for 40 minutes at different temperatures (15, 25, and 35ºC) with solutions with optimum pH values containing 25 mL, 100 mg L^{-1} Pb(II) ion and whether there was any effect of temperature on biosorption.

After every optimization process and equilibrium period, the biosorbent was separated from the solution by centrifuging at 3000 rpm for 5 minutes and the remaining Pb(II) concentration in the solution were analyzed via an AAS (Perkin Elmer Analyst 400 AA). It was determined by the use of acetylene flames.

6.7. Continuous System Biosorption Studies on Removal of Pb(II) by CASB

The Pb(II) removal performance of the CASB was also examined in the dynamic flow system. Flow mode experiments were carried out at 25°C using glass columns (210 mm length and 10.5 mm internal diameter). The biosorbent was filled into the column between two layers of glass wool. To connect solutions to the column, Tygon tubing was used. A multi–channel peristaltic pump (Ismatec IP 8) was used to continuously pump 0.025 L of Pb(II) solutions at pH 5.5 with the flow direction down through each column. The parameters investigated during these studies are the amount of biosorbent (0.01–0.06 g) and the flow rate (0.5–6.0 mL min^{-1}).

Firstly, the flow rate was optimized to identify the column performance of the biochar. During the optimization studies in the continuous system, solutions containing 25 mL of Pb(II) ion at a concentration of 100 mg L^{-1} were used. The 0.03 g of the biochar was packed into the column then the Pb(II) ion solutions were passed through the column by changing the flow rates between 0.5–6.0 mL min^{-1}.

In the optimization of the biosorbent amount in the continuous system, the amount of biosorbent packed into the column at the optimum flow rate (1.0 mL min^{-1}) was changed in the range of 0.01–0.06 g.

Regeneration studies for CASB were carried by the column process under pre–optimized conditions. The EDTA (ethylenediaminetetraacetic acid), HNO_3, and HCl at 0.01 M concentration was used as desorption agents, and performance of the regeneration potential of the biosorbent were investigated in five consecutive cycles. At the end of each cycle, ultrapure water was passed through the column, and the column was washed.

All data obtained in batch and continuous biosorption systems were designed as three independent studies and performed simultaneously, and the results are expressed as the arithmetic means of these studies. While statistical evaluations of the data made with the SPSS 15.0, SigmaPlot 10.0 package program was used in graphic drawing.

6.8. Kinetic models of biosorption

Data on biosorption of Pb(II) ions in the batch system; pseudo–first–order, the pseudo–second–order kinetic models, and intraparticle diffusion model were used to fit equilibrium data using the non–linear form.

6.9. Isotherm models of biosorption

In the isotherm modeling process, the batch system biosorption data of Pb(II) ions were studied by Freundlich, Langmuir, and D–R isotherm models.

6.10. Zeta Potential, FTIR, and SEM-EDX Analysis

The surface charge of the biosorbent was determined by measuring the zeta potential using a zeta sizer (Malvern Zetasizer nano ZS). The pH of solution was adjusted to 1, 2, 3, 4, 5, and 5.5 by adding negligible volumes of 0.1 M HCl and/or 0.1 M NaOH. A Bruker Tensor 27 FTIR spectrophotometer was used to examine the functional groups on the biosorbent surface, at an intensity range of 400–4000 cm^{-1}. KBr disk technique was used by taking IR spectra. A Scanning Electron Microscope (SEM) (Hitachi Regulus 8230 FE–SEM) was used to determine the surface microstructure of the CASB before and after the biosorption of Pb(II). During SEM imaging, also the analysis of EDX was carried out.

6.11. Application Studies

The application potential of CASB in a continuous system was also tested in SW and spiked apple juice samples. Breakthrough curves were obtained and analyzed for synthetic Pb(II) solution and SW.

6.11.1. Application in spiked apple juice

The apple juice sample was purchased from a local market in Eskişehir, Turkey. The biosorption ability of the CASB in apple juice was also tested by the continuous system, as shown in Figure 6.2.

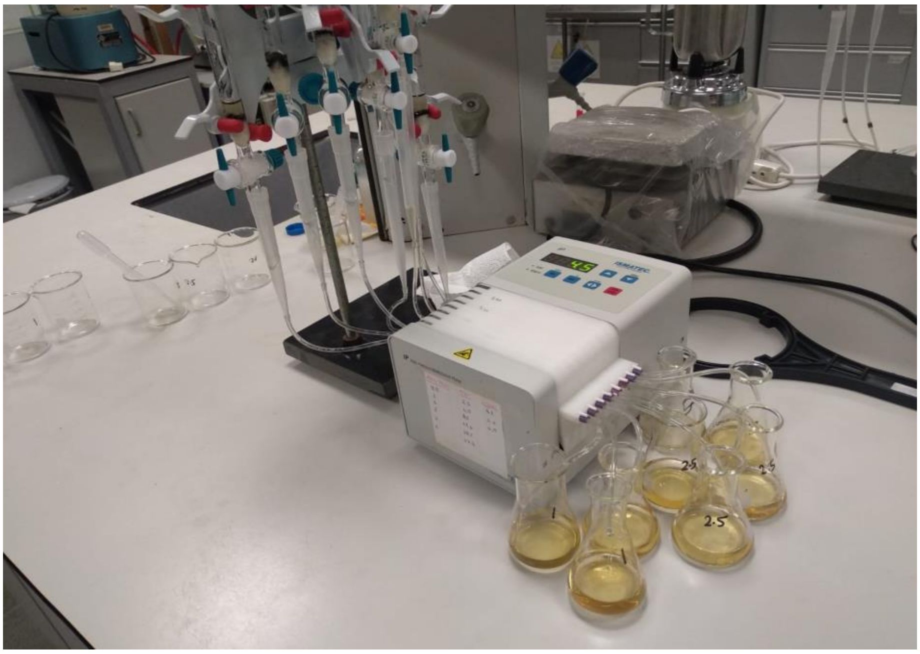

Figure 6.2. Photographs for biosorption of Pb(II) ions by the continuous system in apple juice

The apple juice was diluted with ultrapure water (1:5 dilution). Then, different volumes (1.0, 2.5, 5.0, 7.5, and 10 mL) from the stock solution of Pb(II) at concentration 100 mg L^{-1} were added into diluted apple juice until complete 100 mL of volumetric flasks. The final concentration of Pb(II) ions in the solution was (1.0, 2.5, 5.0, 7.5, and 10 mg L^{-1}). Then, the pH solution was adjusted to 5.5 (optimum pH) by the addition of little drops of HNO_3 or NaOH at a concentration of 0.1 M. The exact 0.030 g (optimum amount) of CASB packed into the column with the optimum flow rate of 1 mL min^{-1}. These solutions passed through the columns as shown in Figure 6.2. Residual concentrations of Pb(II) in the solution was measured by AAS.

6.11.2. Application in simulated wastewater

There are many metals and salts in an aqueous environment, so the effect of these compounds on the Pb(II) biosorption capacity of CASB was evaluated with SW application at 25°C. The following concentrations of various components [Pb(II): 100 mg L^{-1}; Co(II): 5 mg L^{-1}; Ca(II): 5 mg L^{-1}; Cu(II): 5 mg L^{-1}; Mn(II): 5 mg L^{-1}; Zn(II): 5 mg L^{-1}; Na^{+}: 240 mg L^{-1}; NO^{-3}: 10 mg L^{-1}] were used to prepare the SW. The 0.50 g of CASB was weighed accurately. Then, it had been filled into the column between two layers of glass wool. Tygon tubing connections were used to link solutions to the column. A multi−channel peristaltic pump (Ismatec IP 8) was used to continuously pump SW at the flow rate of 1.0 mL min^{-1} direction down through each column.

Breakthrough analyses were performed simultaneously for both synthetic Pb(II) solution at 100 mg L^{-1} and SW.

7. RESULTS AND DISSCUSION

7.1. Batch System Studies

The batch system biosorption studies have optimized the factors affecting on the biosorption. In the light of parameters such as pH, biomass dosage, and contact time, the biosorption process has been optimized. Besides, the influence of ionic strength on Pb(II) biosorption of CASB was studied. The batch biosorption data were evaluated through the kinetic and isotherm models.

7.1.1. Effect of initial pH

The initial pH value of the medium is among the key factors affecting the biosorption performance of biosorbent materials. The effect of pH on the Pb(II) biosorption onto CASB was given in Figure 7.1.

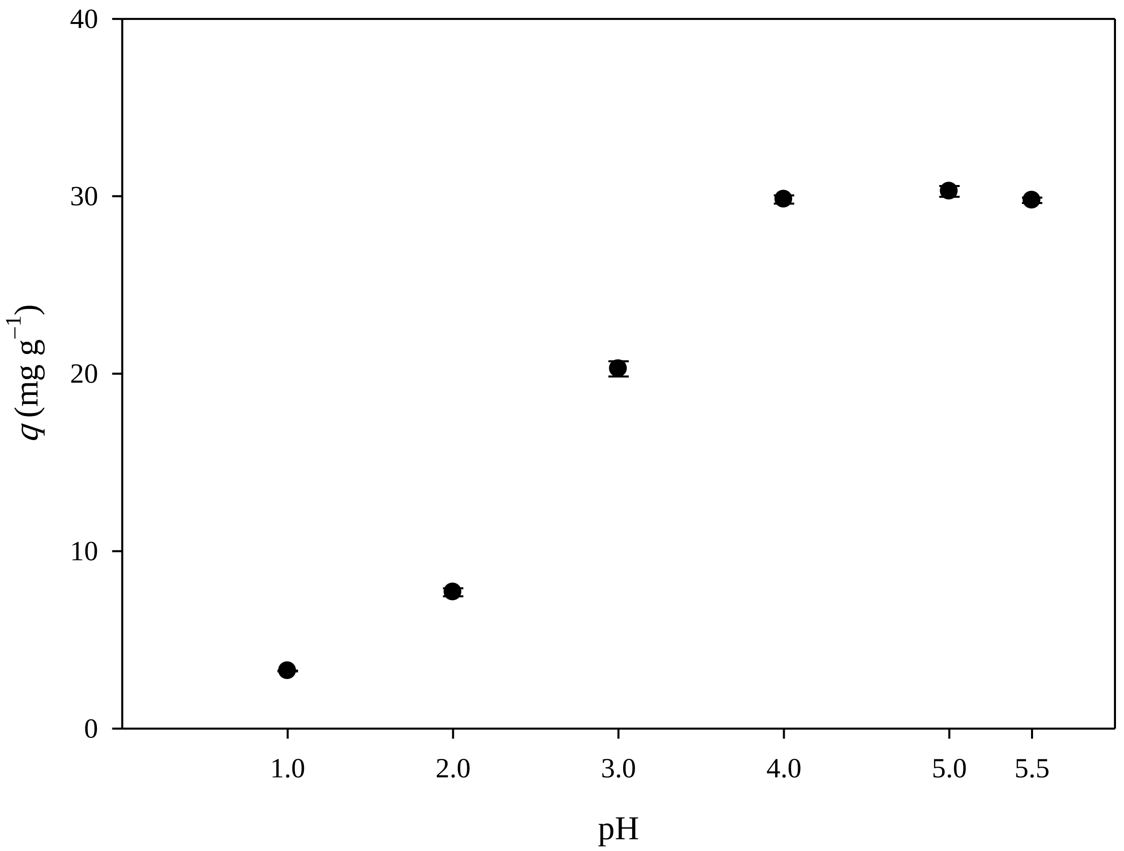

Figure 7.1. Effect of solution pH on biosorption of Pb (II) onto CASB (Pb(II) concentration: 100 mg L^{-1}; CASB dosage: 0.050 g; contact time: 60 min; agitation rate: 250 rpm temperature: 25 ± 1°C)

According to Figure 7.1, almost little biosorption has occurred at low pH values such as 1.0–2.0. Due to the high concentration of H$^+$ ions in acidic conditions, the binding sites that provide biosorption on the biosorbent surface protonated, and this prevents Pb(II) ions from binding to these regions. It was observed that the biosorption capacities showed a sharp increase between pH 2.0 and 3.0. The highest values of the biosorption capacities were recorded in the pH range of 4.0–5.5. Experiments were performed with pH values of up to 5.5 based on the fact at higher pH values, the precipitation of metal occurred, and deterioration of biosorbent or interfered with the accumulation (Gadd and Gadd, 1988; Niu et al., 1993; Puranik and Paknikar, 1997; Park et al., 2020). Thus, the optimum pH value was determined as 5.5 and in subsequent Pb(II) biosorption studies, solutions with a pH of about 5.5 were used. That means that there is an advantage, which is to use the solution directly as it is without adjusting its pH during the biosorption process. Similar literature findings were reported by (Ahmad et al., 2018; Wang et al., 2018c).

Zeta potential values for biochar have been measured as a function of the solution pH. Isoelectric point of CASB (pH_{IEP}) was determined based on the zeta potentials at various pH conditions for the solution. Zeta potentials of CASB at various pH values was given in Figure 7.2.

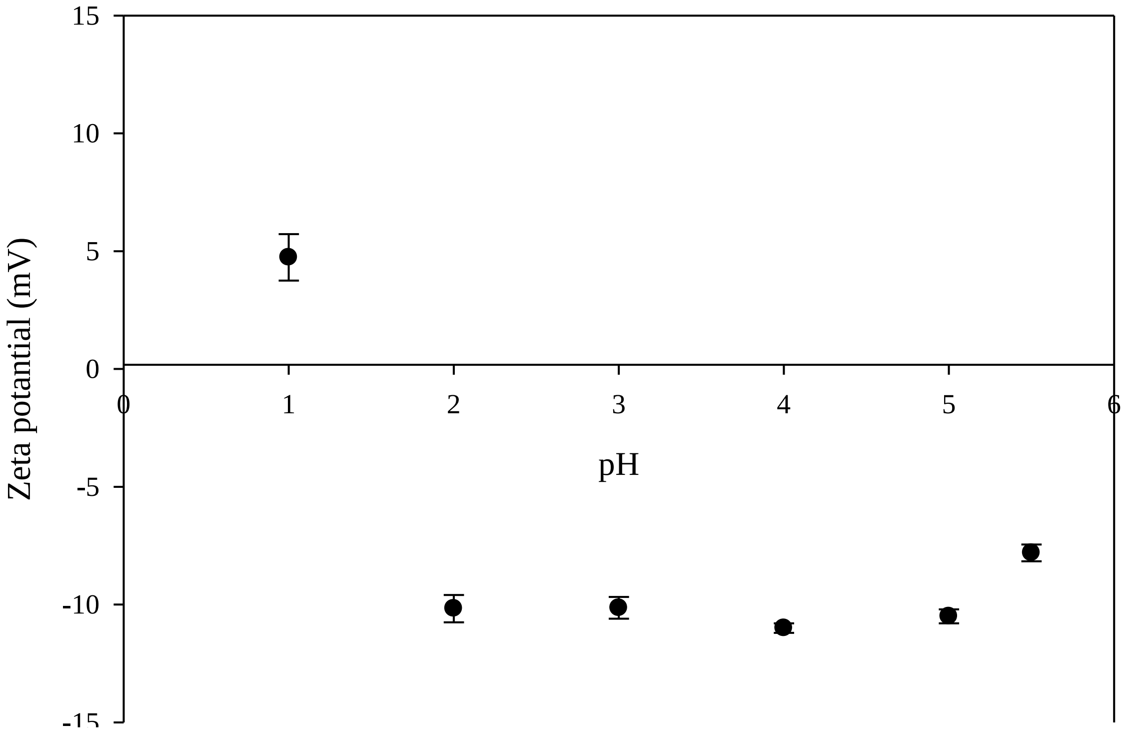

Figure 7.2. Zeta potentials of CASB at various pH values

Figure 7.2, indicated the zeta potential of the CASB decreased significantly from +4.73 mV at pH 1.0 to −10.17 mV at pH 2 and then remained constant around −10 mV. This indicates that the particles in the biochar carried negative charges on their surfaces throughout the most examined pH range, and the pH_{IEP} is approximately 1.3. Similar findings have been reported by (Pan et al., 2013; Ding et al., 2016).

When the pH was higher than pH_{IEP}, the biosorbent surface was negatively charged due to the deprotonation of the hydrated surface of CASB. Thus, an increase in the electrostatic attraction between the biosorbent surface and Pb(II) ions caused the Pb(II) ions to become strongly biosorbed. In contrast, when the pH was lower than pH_{IEP}, the surface is charged positively due to the protonation of the hydrated CASB surface, which could be responsible for the lower biosorption capacity (Wang et al., 2019).

7.1.2. Effect of biosorbent dosage

Determination of the most appropriate amount of biosorbent to be used is another parameter that plays a critical role in effective pollutant removal, process efficiency and economy. Since an increase in the removal of Pb(II) ions is directly proportional to the number of active binding regions of the biosorbent, the amount of biosorbent has a major impact on the process of biosorption. The effect of the CASB dosage on the biosorption of Pb(II) is given in Figure 7.3.

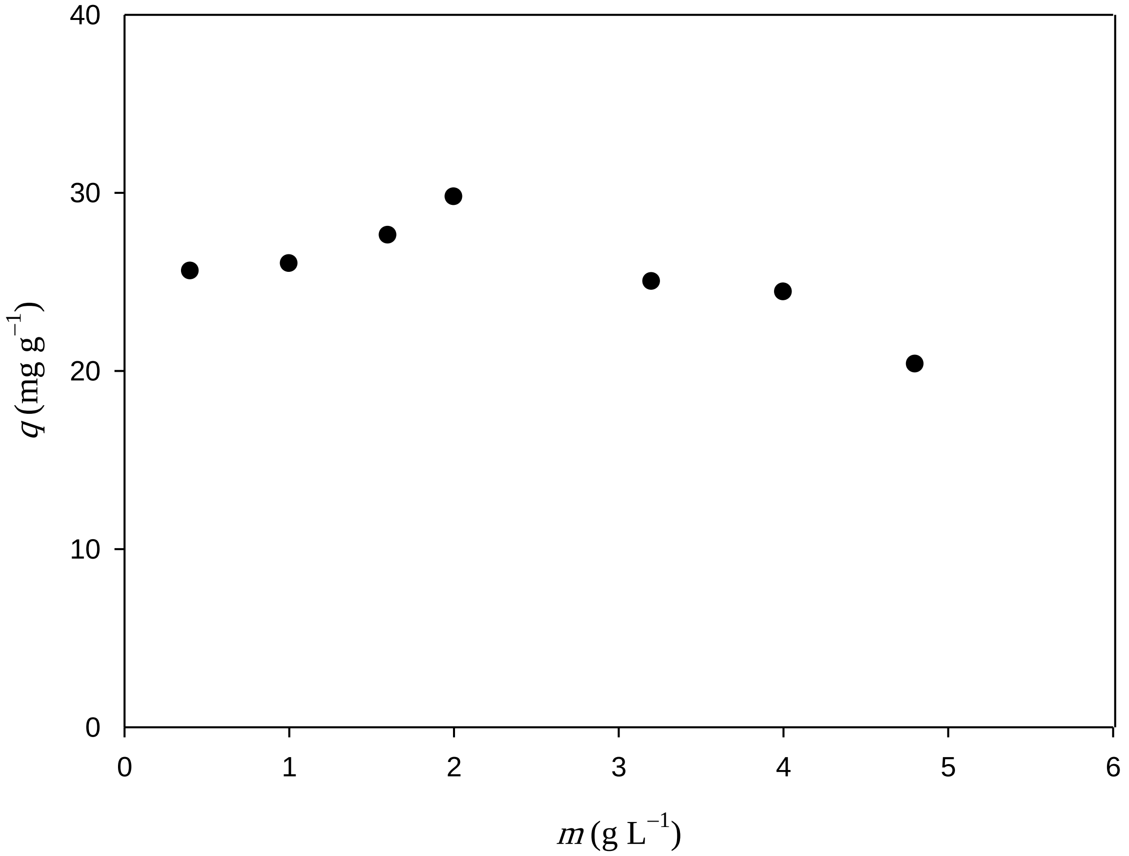

Figure 7.3. Effect of biosorbent dosage on the biosorption of Pb(II) onto CASB

According to the results given in Figure 7.3, the biosorption capacity of CASB for Pb(II) increased with increasing amounts of biosorbent in the range of (0.4–2.0) g L^{-1} ($p < 0.05$). This increase in biosorption performance explained by the fact that more binding sites provided due to increased biosorbent surface area (Zubair et al., 2008). It is noted after 2.0 g L^{-1} the biosorption capacity decreased. Similar findings were reported by (Zubair et al., 2008; Liang et al., 2017). The optimum sorbent dosage in our study was recorded as 2.0 g L^{-1} and subsequent studies were continued with the optimum amount of CASB. The biosorption capacity of biochar at the optimum sorbent amount was noted as 29.77 mg g^{-1}. The previous findings indicated that the biosorption yield of the raw biomass of *C. annuum* L. at this point was 48.87%. This yield corresponded to a biosorption capacity of 28.72 mg g^{-1} (Özcan et al., 2007). This observation showed that the Pb(II) biosorption capacity of CASB at 2.0 g L^{-1} was slightly higher than the raw biomass.

On the other hand, different reasons have been proposed to explain the decreased sorption capacity at increased biomass, including that of the electrostatic interactions, interference between functional groups, availability of solute, and decreased mixing at higher biomass levels (Meikle et al., 1990; Fourest and Roux, 1992).

7.1.3. Effect of contact time and biosorption kinetics

Figure 7.4 shows the impact of contact time and the predicted kinetic in the range 5–75 min on the Pb(II) biosorption capacity of CASB.

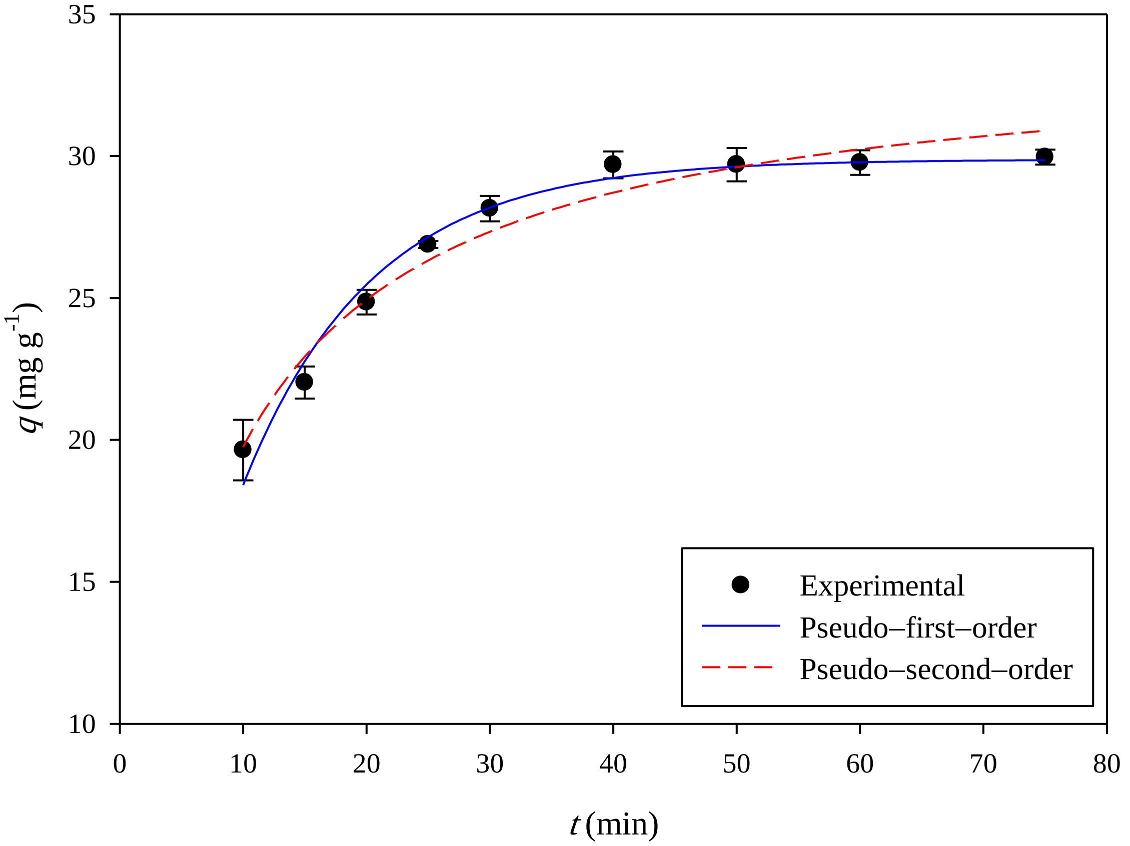

Figure 7.4. Experimental data and the predicted kinetic curves for Pb (II) sorption by CASB

According to these data, it can be said that Pb(II) biosorption capacity of CASB is fast and reaches equilibrium within 40 min. No significant change in Pb(II) removal capacity of the CASB observed after this equilibrium time ($p > 0.05$). This rapid biosorption may be associated with an abundance of active binding sites present on the CASB surface. Then, an increase in contact time, it will be difficult to occupy the remaining vacant sites because of the repulsive forces on solid and liquid phases between the Pb(II) ions (Saeed et al., 2005a; Saeed et al., 2005b). Short equilibrium times in biosorption applications for water treatment are an important feature for industrial–scale applications of the proposed biosorbent. For example, it has been reported that 1h of time is sufficient for equilibrium for Pb(II) biosorption onto biochars obtained from sugarcane bagasse at 500 and 600°C (Ding et al., 2014). In the other studies related to this subject, it was shown that the Pb(II) ions biosorption onto biochars obtained from sugar cane bagasse and orange peel reached the highest removal efficiencies within 30 min for sugar cane bagasse biochar and 15 min for orange peel biochar (Abdelhafez and Li, 2016). These selected examples represent the studies carried out in the short duration of the biosorption equilibrium. However, the equilibrium time in our study is quite short, and it provides an important advantage for the biochar we recommend.

The biosorption kinetics of Pb(II) ions onto CASB were evaluated by employing the pseudo–first–order and the pseudo–second–order kinetic models and results plotted in Figure 7.4

The parameters and r^2 values of those kinetical models for Pb(II) biosorption was given in Table 7.1.

Table 7.1. Kinetic parameters for the biosorption of Pb(II) onto CASB

Pseudo–first–order			
Parameter		*t*	*p*
q_e (mg g^{-1})	29.878	91.563	<0.0001
k_1 (min^{-1})	9.57×10^{-2}	21.7669	<0.0001
r^2: 0.976; *S.E.*: 0.629; *F*: 284.05			

Table 7.1. Kinetic parameters for the biosorption of Pb(II) onto CASB (continued)

Pseudo–second–order			
Parameter		*t*	*p*
q_e (mg g^{-1})	33.817	12.071	0.0001
k_2 (g mg^{-1} min^{-1})	4.15×10^{-3}	9.908	0.0004
r^2: 0.966; *S.E.*: 0.745; *F*: 200.74			

The obtained r^2 values indicated that Pb(II) biosorption onto CASB was the most suited to the pseudo–first–order kinetic model.

7.1.4. Biosorption isotherm

Langmuir, Freundlich, and D–R isotherm models for removal of Pb(II) ions onto CASB at 25°C as given in Figure 7.5.

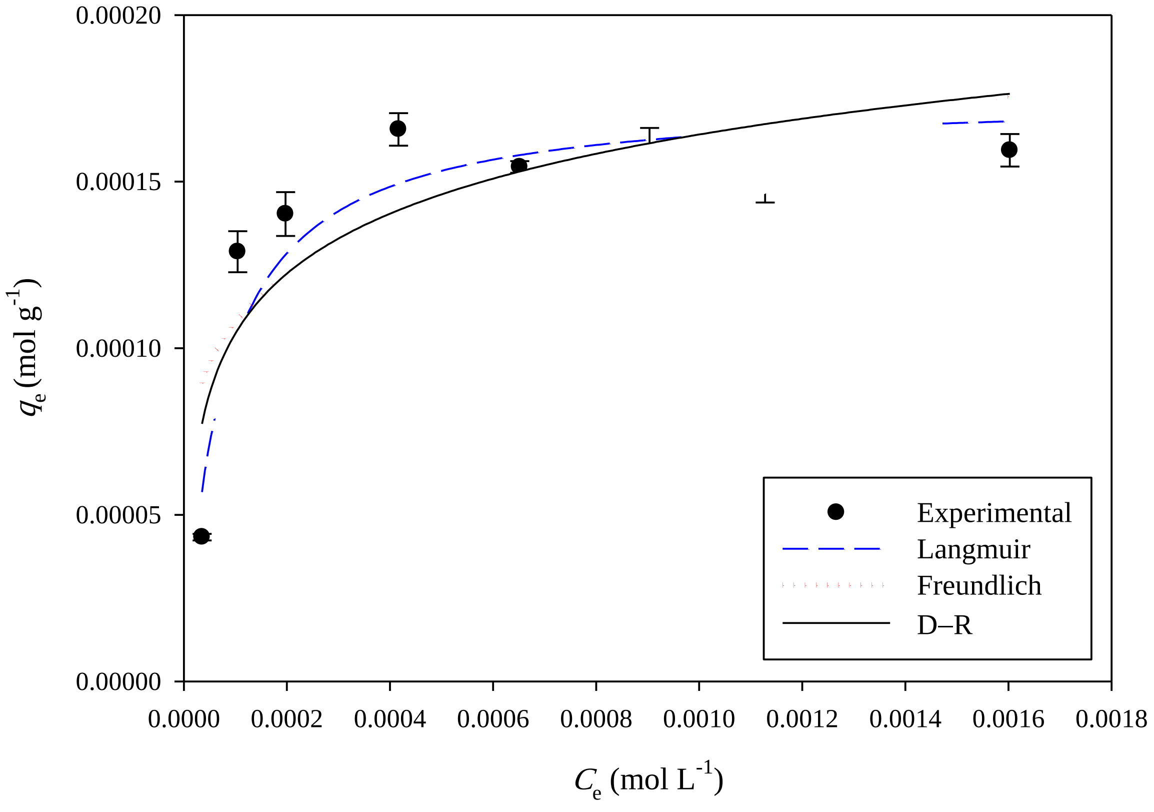

Figure 7.5. Biosorption isotherms of Pb(II) on CASB

Figure 7.5 and data related to the relevant isotherm parameters presented in Table 7.2.

Table 7.2. Isotherm parameters for the biosorption of Pb(II) onto CASB

Langmuir isotherm

Parameter		*t*	*p*
$q_{\max}$ (mol g^{-1})	1.758x10^{-4}	4.458	0.0043
K_L (L mol^{-1})	1.357x10^{4}	3.784	0.0091
r^2: 0.926; *S.E.*: 1.5x10^{-3}; *F*: 75.348			

Freundlich isotherm

Parameter		*t*	*p*
n	5.669	2.760	0.0329
K_F (L g^{-1})	5x10^{-3}	2.077	0.0830
r^2: 0.637; *S.E.*: 2.605x10^{-5}; *F*: 10.537			

D–R isotherm

Parameter		*t*	*p*
$q_{\max}$ (mol g^{-1})	3x10^{-4}	6.535	0.0006
ß (mol^2 kJ^{-2})	5.093x10^{-3}	3.954	0.0075
E (kJ mol^{-1})	9.908		
r^2: 0.723; *S.E:* 2.278x10^{-5}; *F*: 15.635			

The r^2 values in Table 7.2 show that biosorption onto CASB matched well with the Langmuir isotherm model non–linear form. Compliance with the Langmuir isotherm model indicates that biosorption was taken place on a homogeneous biosorbent surface with a monolayer. The maximum monolayer biosorption capacity for removal of Pb(II) by CASB was 36.43 mg g^{-1} under optimized conditions. The constants of the D–R isotherm model were arranged in Table 7.2. This model has a relatively high r^2 value after the Langmuir model. If E = 8–16 kJ mol^{-1}, then the chemical ion–exchange is responsible for the reaction (Helfferich, 1962); if $E < 8$ kJ mol^{-1}, then physical biosorption occurs (Onyango et al., 2004). The calculated E value of the biosorption was found to be 9.91 kJ mol^{-1}. This value is in the 8–16 kJ mol^{-1} range, indicating that chemical ion–exchange may also be involved in the Pb(II) biosorption onto CASB.

In the literature, the biosorption capacity values of different biochar feedstocks are given comparatively from time to time in removing Pb(II) pollutants. Considering that the compared capacity values are generally the values of the studies carried out under different experimental conditions, so these comparisons are not very meaningful, but they provide an idea for practical use. Therefore, Table 7.3 compared to the maximum biosorption capacity values of lead removal by CASB feedstock and various biochar feedstocks in the literature.

Table 7.3. Different biochar feedstock, which used for biosorption of Pb(II) in aqueous media reported in studies with maximum biosorption capacity

Type of biochars	**Pre/ Treatment**	**Maximum biosorption capacity (mg g^{-1})**	**References**
Pinewood biochar	Hydrothermal	4.25	(Liu and Zhang, 2009)
Rice husk biochar		2.40	
Oak wood biochar	Auger reactor, air drying, crushing, and sieving	2.62	(Mohan et al., 2007)
Pine bark biochar		3.00	
Oak bark biochar		13.10	
Sugarcane bagasse biochar	Aerobically digesting, crushing, and sieving	6.54	(Inyang et al., 2011)
Pomelo peel biochar	Drying and impregnating with 85% (wt%) H_3PO_4	88.7	(Zhao et al., 2018)
Sewage sludge biochar	Drying and sieving	30.88	(Lu et al., 2012)
Peanut shell biochar	Washing, drying, milling, and sieving	36	(Wan et al., 2018)
Peanut hull biochar	Drying	22.82	(Xue et al., 2012)
Maple wood biochar	Drying	43.3	(Wang et al., 2018b)

Table 7.3. Different biochar feedstock, which used for biosorption of Pb(II) in aqueous media reported in studies with maximum biosorption capacity (continued)

Pecan nutshell biochar	Drying and milling	80.3	(Duran-Jimenez et al., 2017)
Root of rose biochar	Oven drying	52.95	(Khare et al., 2017)
Pear tree waste biochar	Crushing, sieving, and drying	26.2	(Park et al., 2015)
Swine sludge biochar	Pyrolysis	119.63	(Liu et al., 2020)
Sewage sludge biochar	Modification by KOH	57.48	(Zhang et al., 2019a)
Acorus calamus Linn. and feather wast biochar	Impregnating in phosphoric acid and heating at 500°C	56.64	(Yin et al., 2019)
Sugar cane bagasse biochar	Washing, drying, and pyrolysis	86.96	(Abdelhafez and Li, 2016)
Orange peel biochar		27.86	
CASB	Pyrolysis	36.43	This study

7.1.5. Effect of ionic strength

The ionic strength impact on Pb(II) biosorption onto CASB was investigated by varying the concentration of KNO_3 from 0.02 mol L^{-1} to 0.20 mol L^{-1} at room temperature. Effect of salt concentration on Pb(II) biosorption by CASB Figure 7.6.

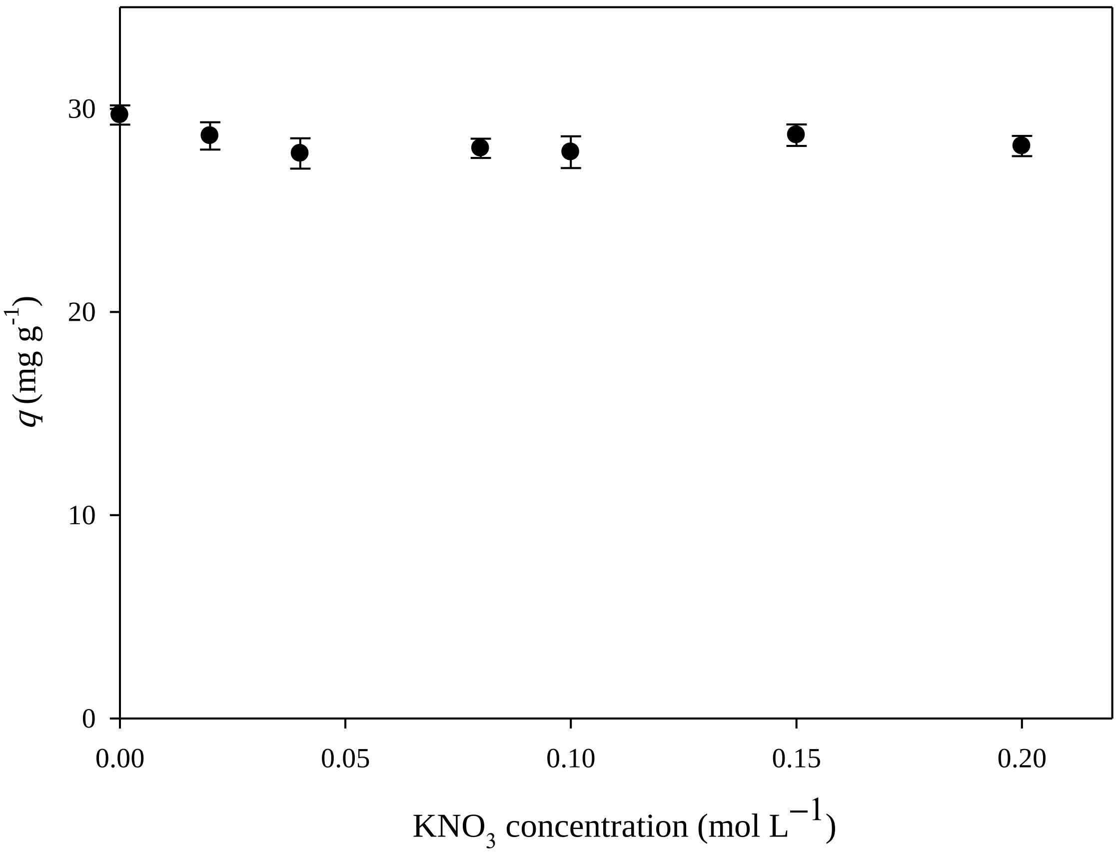

Figure 7.6. Effect of salt concentration on Pb(II) biosorption onto CASB

Figure 7.6 demonstrated that the ionic strength had no noticeable impact on the biosorption capacity of CASB. When KNO_3 concentrations increased from 0.00 to 0.20 mol L^{-1} led to a slightly decreased in the biosorption capacity of CASB from 29.69 to 28.16 mg g^{-1}, respectively. The absence of the effectiveness of salt on the biosorption capacity of CASB is considered another essential feature for the accessibility of a large–scale application of the proposed biochar in a medium containing salt.

7.2. Continuous Flow System Studies

To design the biosorption process on an industrial scale, continuous system biosorption designed at a laboratory scale is of great importance. The use of packed bed columns is important for both wastewater treatment applications and making the biosorbent more efficient, but it is more suitable for use on an industrial scale. It is also possible to achieve high biosorption efficiencies in a continuous system (Sağ et al., 2000).

7.2.1. Effect of flow rate on Pb(II) biosorption

The main advantage for a submitted biosorbent materials to investigate their technical feasibility in applications in wastewater treatment was the continuous flow mode biosorption possibility. The biosorption of various pollutants like metals, carbofuran, and phosphates by biochar derived from several biomass feedstocks has been observed as an inverse relationship between flow rate and biosorption capacity (Kizito et al., 2016; Mondal et al., 2016; Jung et al., 2017).

The impact of flow rate on Pb(II) biosorption for the CASB was examined at different flow rates (0.5, 1.0, 2.0, 4.0, and 6.0 mL min^{-1}). The effect of flow rate on the biosorption of Pb(II) onto CASB in a continuous system are shown in Figure 7.7.

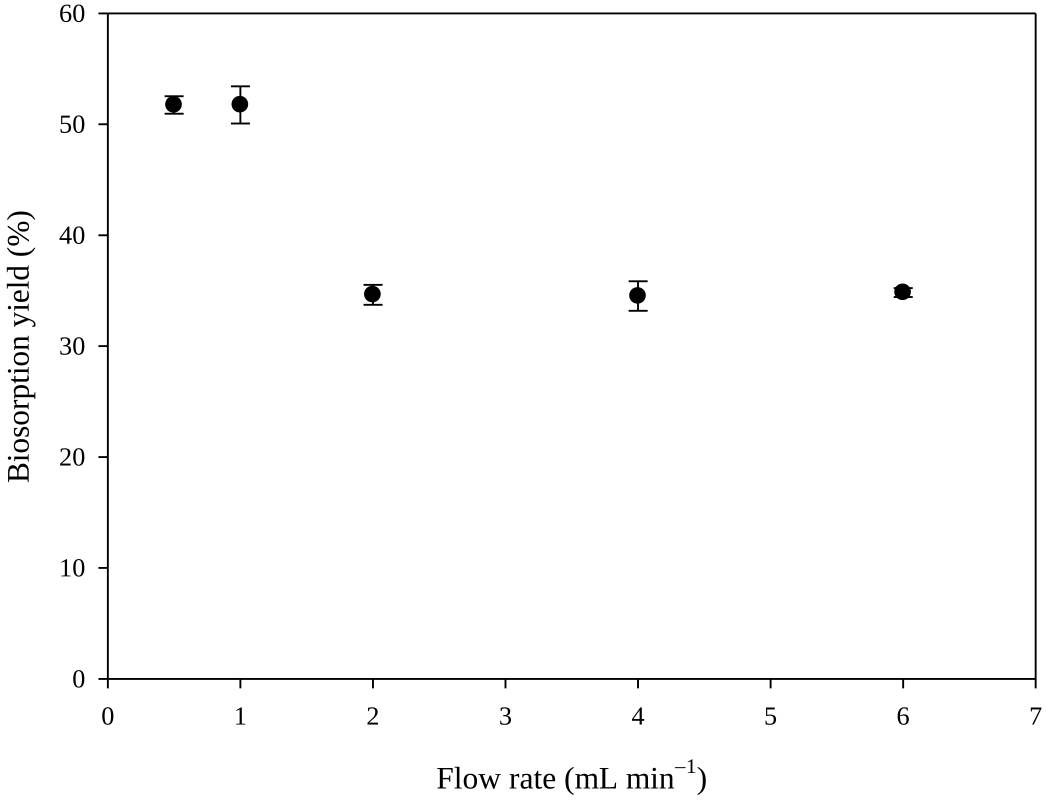

Figure 7.7. Effect of flow rate on Pb(II) biosorption onto CASB in a continuous system

The biosorption yield of CASB at a flow rate of 0.5 ml min^{-1} was measured as 51.73 ± 0.79%. When the flow rate of metal solution increased from 1.0 to 2.0 mL min^{-1} the biosorption yield of CASB reduced from 51.75 ± 1.68% to 34.63 ± 0.89% ($p < 0.05$) and then remained almost constant ($p > 0.05$). The explanation for this behaviour is the lower contact time between Pb(II) ions and biosorbent surface at higher flow rates. Conversely, slow flows allow a higher contact time to make the diffusion more effective into the pores (Rosales et al., 2017). At a lower flow rate, Pb(II) ions have a longer interaction with binding sites of CASB, which results in higher biosorption yields. In our study, the highest biosorption efficiency was achieved for Pb(II) ions at a flow rate of 1.0 mL min^{-1}, then later continuous system experiments were carried out at this flow rate.

7.2.2. Effect of CASB dosage on Pb(II) biosorption

The influence of the amount of CASB on the Pb(II) biosorption in the continuous system analyzed by packing the amounts of CASB into the column in the range of 0.01–0.06 g and comparing these amounts with the biosorption efficiency. The effect of biosorbent dosage on the biosorption of Pb(II) onto CASB in a continuous system the are given in Figure 7.8.

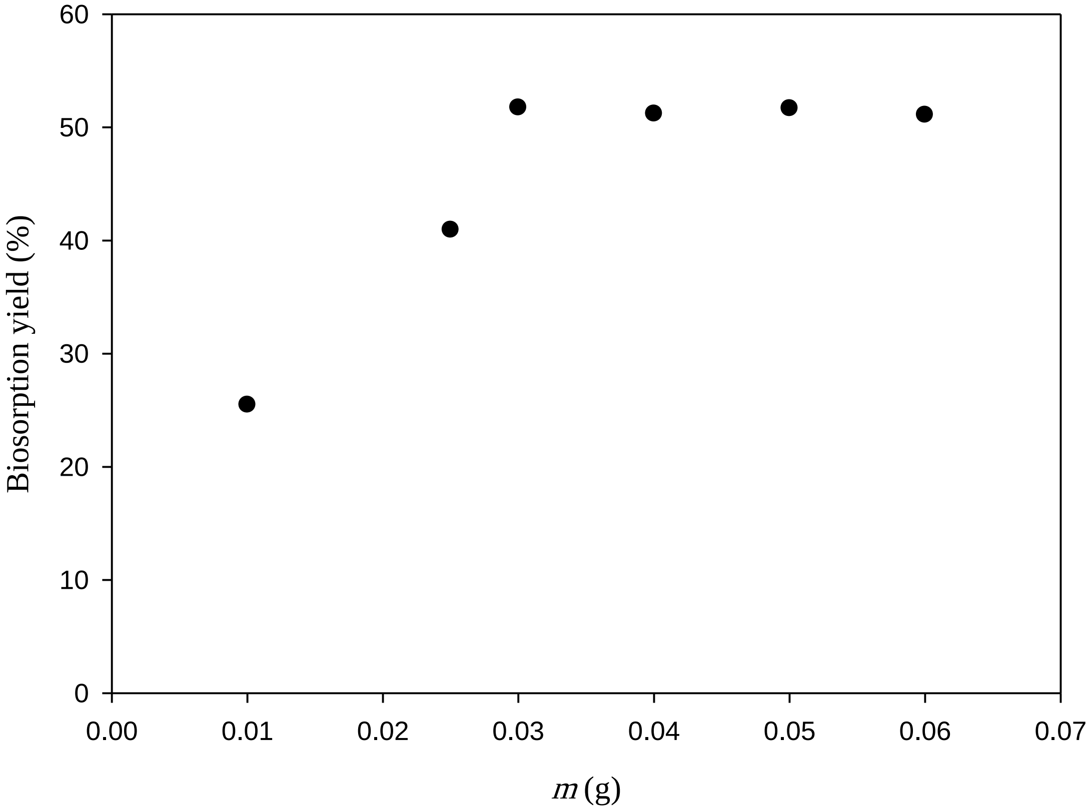

Figure 7.8. Effect of biosorbent dosage on the biosorption of Pb(II) onto CASB in a continuous system

When the dosage of CASB filled in the column increased from 0.01 to 0.03 g, the Pb(II) biosorption yield increased from 25.47 ± 0.80% to 51.75 ± 1.68% ($p < 0.05$) and stayed almost constant ($p > 0.05$). The higher bed heights give further binding sites for Pb(II)–CASB interactions. This can clarify the high biosorption yields at higher amounts of CASB in the continuous flow system. The constant biosorption trend in the second stage can be explained by the saturation of the binding sites on the CASB surface.

7.2.3. Desorption performance and reusability of CASB

The desorption ability of a biomass allows it to be used repeatedly in the biosorption process and to recover metal ions. This makes the process economical also in industrial applications. Result of regeneration potential of CASB in the Pb(II) biosorption in Figure 7.9.

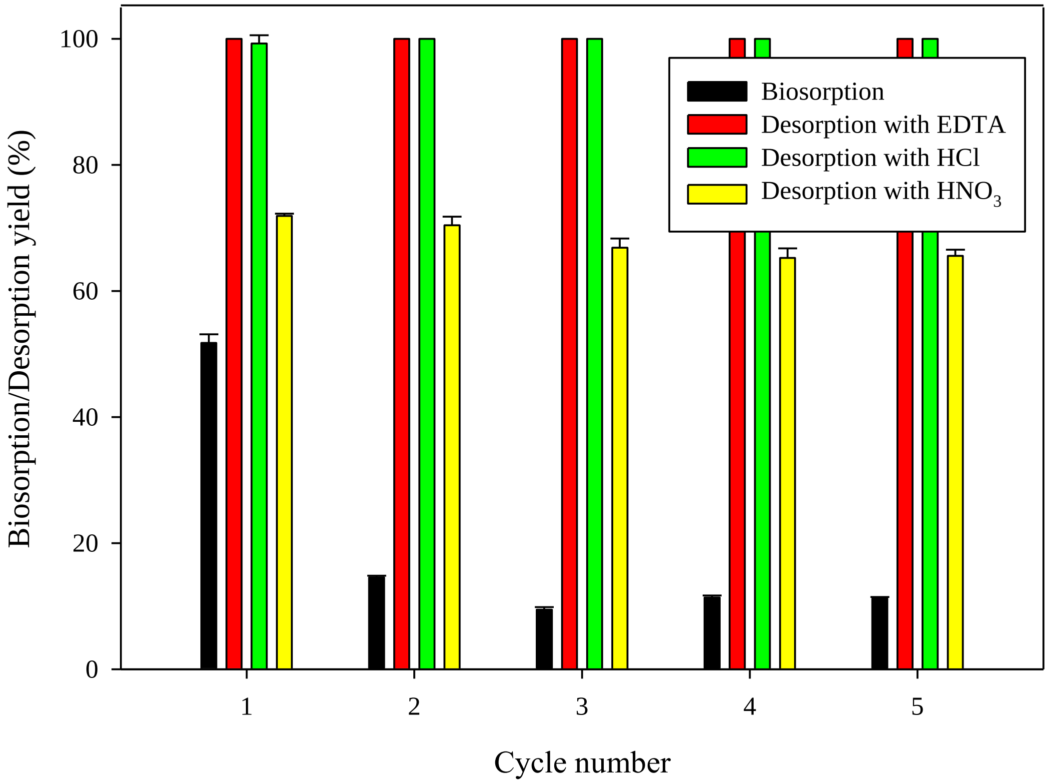

Figure 7.9. Regeneration potential of CASB in the Pb(II) biosorption

Regeneration tests of EDTA, HCl, and HNO_3 solutions were designed to identify the nature of the reusability of CASB in the continuous system for 5 consecutive cycles. After the each regeneration cycle, CASB was washed with ultrapure water. The biosorption efficiency of CASB for Pb(II) dropped significantly from 51.75 to 14.58% after the first cycle and after remained constant. The lower biosorption yields after the first cycle can be ascribed to the degeneration of the biochar structure due to the treatment with these eluents. Loaded Pb(II) ions could be completely eluted using 0.01 M EDTA and 0.01 M HCl in all cycles.

7.3. Application the Biosorption Studies

7.3.1. Application in spiked apple juice

The biosorption ability of the CASB in apple juice was also tested by the continuous system. The biosorption yields of CASB in spiked apple juice samples were given in Figure 7.10.

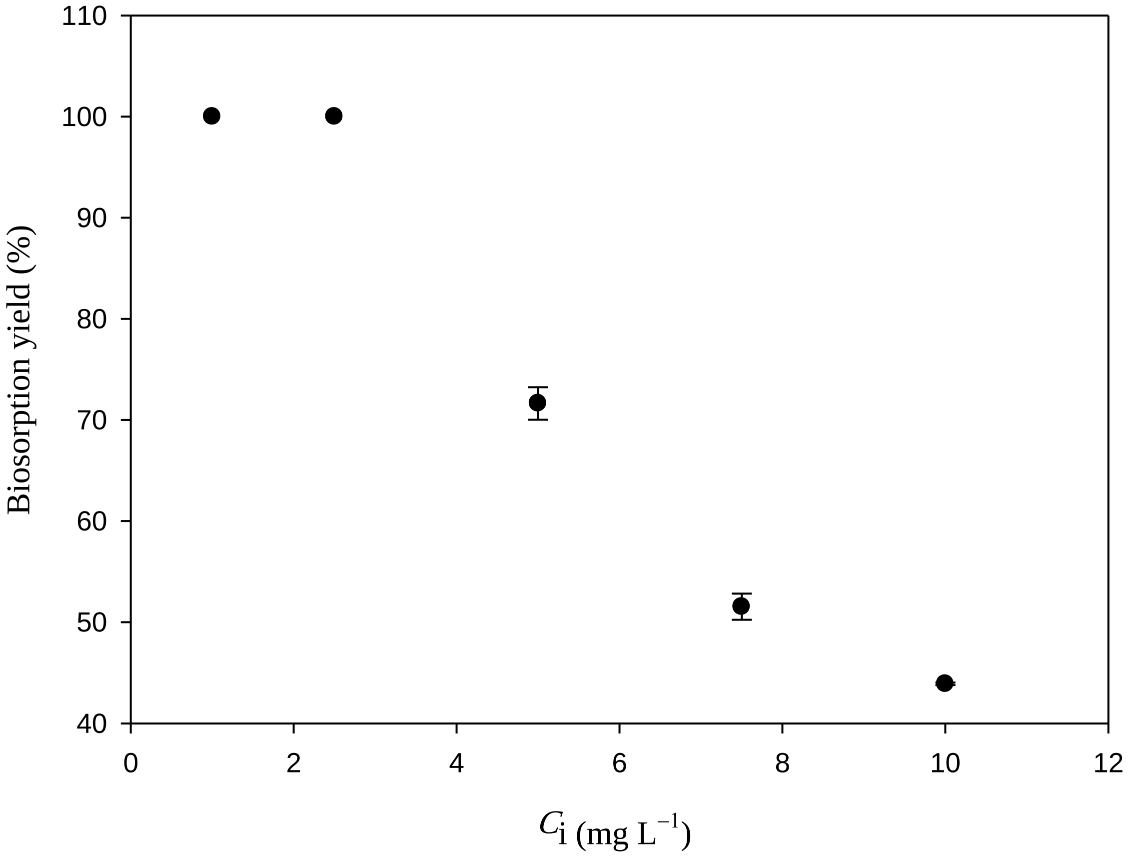

Figure 7.10. Biosorption of Pb(II) ions by the continuous system in apple juice

As can be seen in Figure 7.10, the biosorption yield for Pb(II) onto CASB reached 100% in samples of apple juice containing Pb(II) at concentrations of 1.0 and 2.5 mg L^{-1}. When the Pb(II) concentration in the sample was increased to 10.0 mg L^{-1} the biosorption performance of CASB decreased to 43.91%. A similar tendency was reported for Pb(II) removal from apple juice samples using magnetic nanoparticles functionalized lactic acid bacteria cells (Li et al., 2020). The findings in the application part of our study showed that this proposed new biochar can be used in the treatment of contaminated fruit juices, in addition to its usability in wastewater treatment.

7.3.2. Application in simulated wastewater

The ability of the packed beds for biosorption is generally described by the breakthrough curves (Akar et al., 2018). Breakthrough studies were performed at the same conditions simultaneously for both SW and synthetic Pb(II) solution (100 mg L^{-1}) and the breakthrough curves are given in Figure 7.11. The amount of CASB, influential Pb(II) concentration, bed depth, and the flow rate was 0.50 g, 100 mg L^{-1}, 1.0 cm, and 1 mL min^{-1}, respectively.

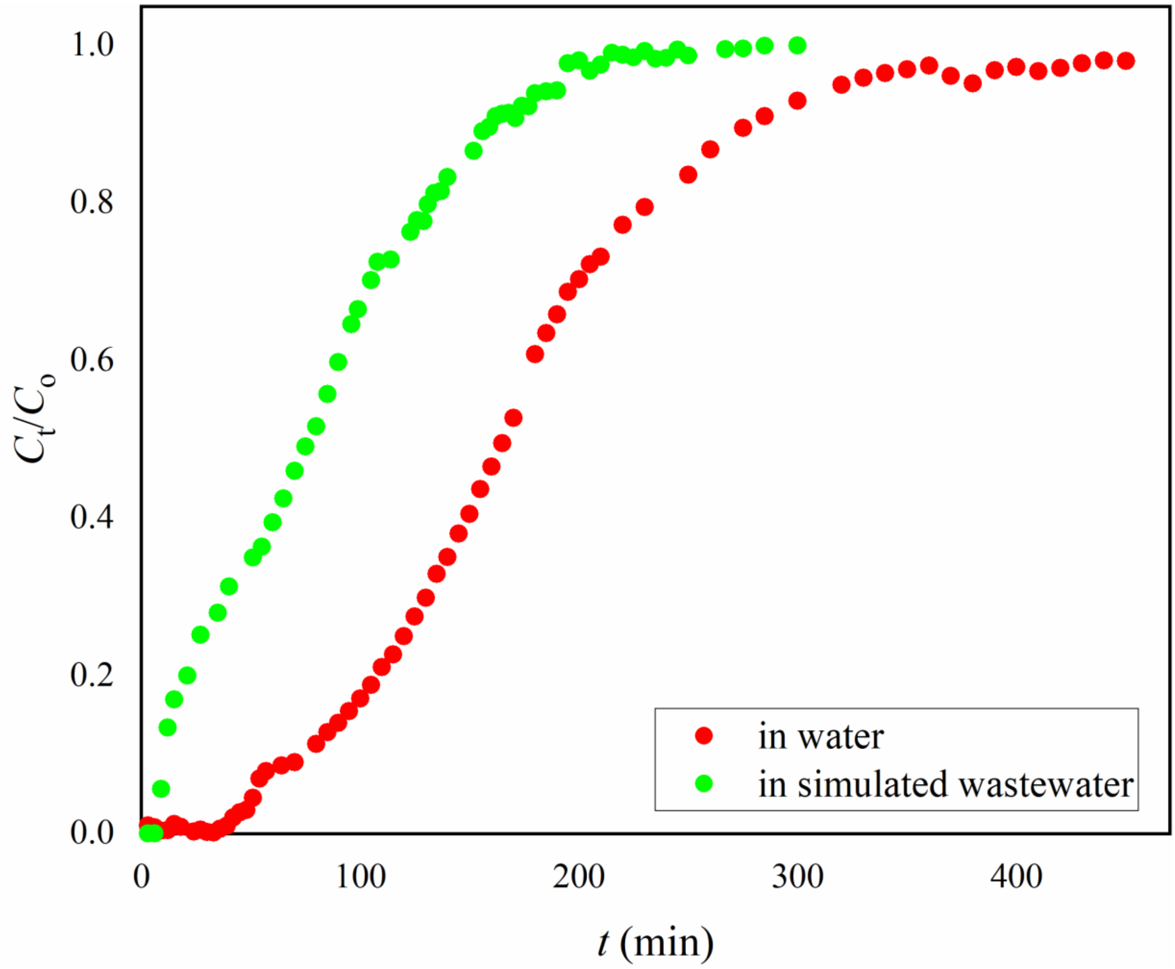

Figure 7.11. Breakthrough curve for Pb(II) biosorption by CASB by column system

As can be seen in Figure 7.11, effective biosorption of Pb(II) onto CASB was reported until the breakthrough time (t_b: 54 and 9 min in synthetic Pb(II) solution and SW, respectively), and the curve slope was reduced after the exhaustion time (t_e: 320 and 195 min in synthetic Pb(II) solution and SW, respectively). These values may be explained by exist competition between Pb(II) and other metals in SW, so the t_b and t_e for SW lower than for synthetic Pb(II) solution. A similar tendency was reported by (Yan et al., 2018).

7.4. Characterization Studies

7.4.1. FTIR analysis

Figure 7.12 shows representative FTIR spectrum of CASB before and after Pb(II) biosorption.

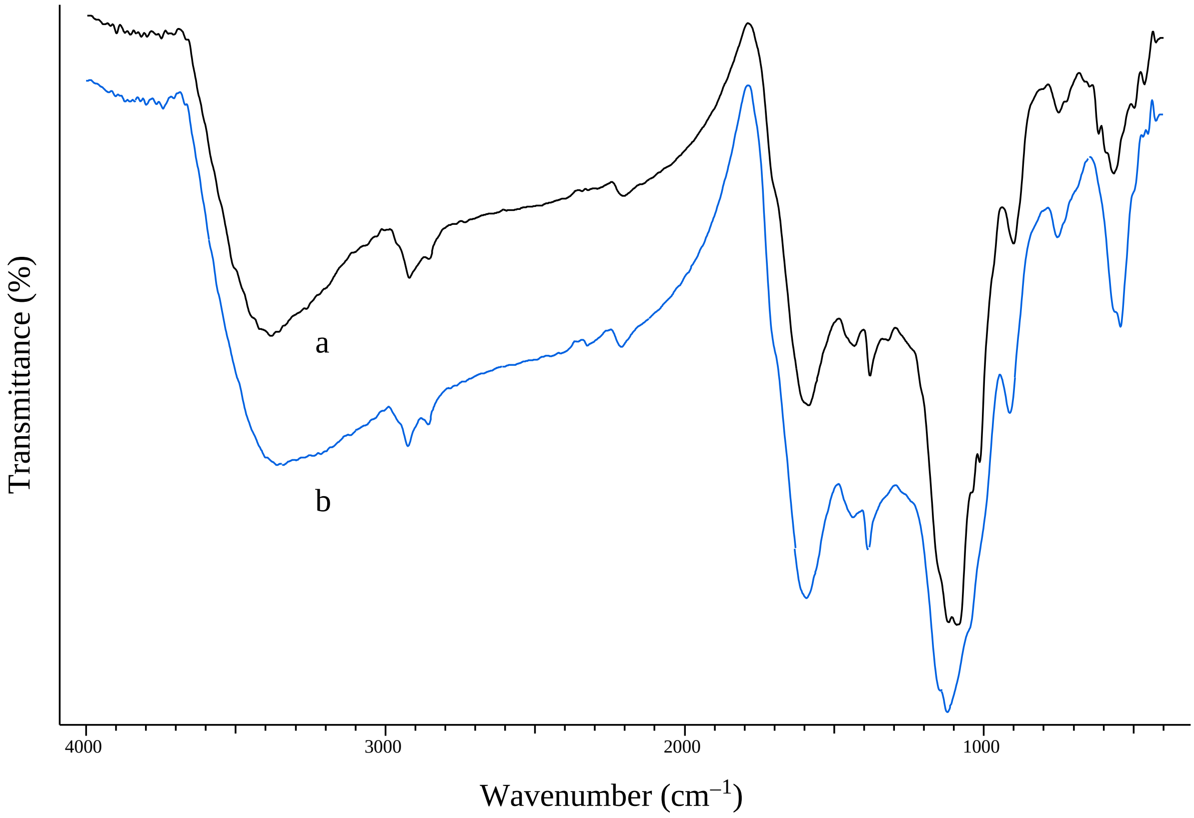

Figure 7.12. FTIR spectrum of CASB before (a) and after Pb(II) biosorption (b)

Figure 7.12 shows the IR spectra of CASB and Pb(II) loaded CASB in transmission mode from 4000–400 cm^{-1} wavenumber. In the spectrum of CASB, peaks were observed at 3381, 2918, 2855, 1585, 1433, 1381, 1319, 1118, 1092, 901, 750, 617, 567, and 498 cm^{-1}. As seen in Figure 7.12, the CASB surface is rich in functional groups containing C, O, and H elements (Zhang et al., 2016a). After the Pb(II) removal process, the position of the bands corresponding to –OH and –NH groups (3381 cm^{-1}), and C–O groups (1092–1119 cm^{-1}) shifted. Intensities of these peaks also decreased. The peaks between 1000–400 cm^{-1} are belonging to C–H groups inside the aromatic rings (Kizito et al., 2017). The peak at 901 cm^{-1} in this range shifted to 908 cm^{-1}, while the peaks at 617, 567, and 498 cm^{-1} turned into a single peak at 542 cm^{-1} with a slight intensity increase. These findings confirm the importance of these functional groups for the uptake of Pb(II) by CABS.

7.4.2. SEM-EDX analysis

The characterization of the surface morphology of CASB and CASB–Pb(II) was also performed using SEM and EDS analysis as shown in Figure 7.13.

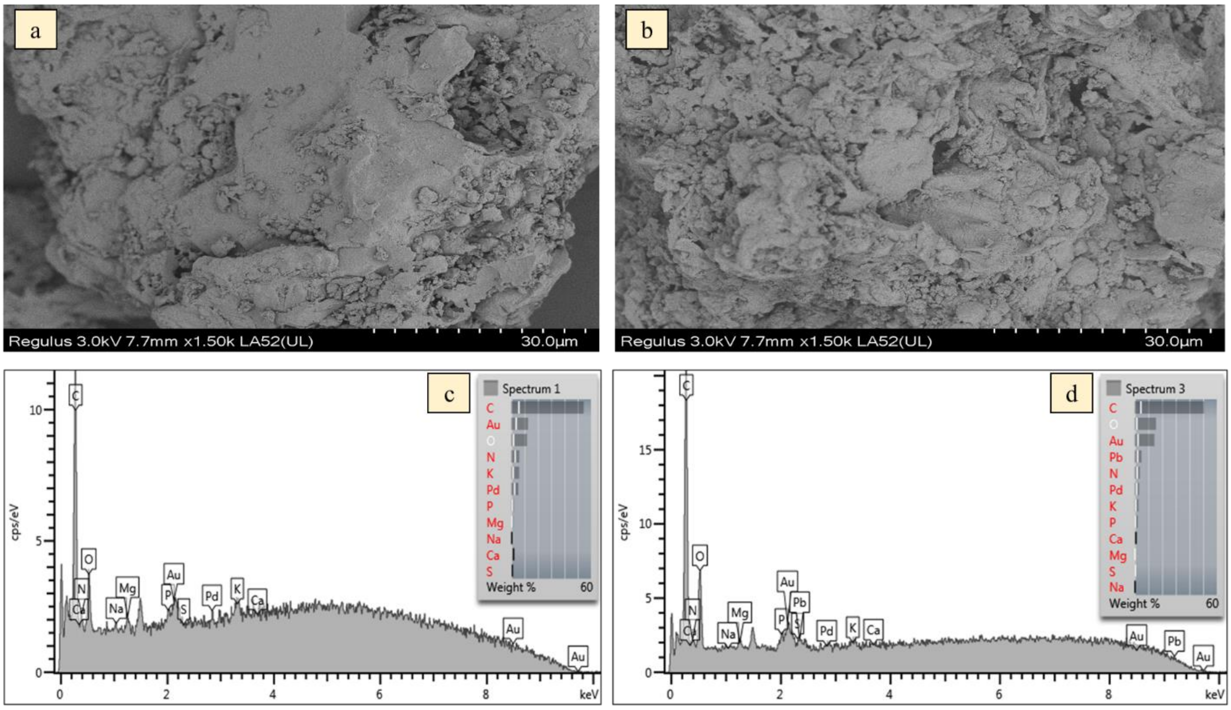

Figure 7.13. SEM image of CASB before (a) and after (b) biosorption of Pb(II) ions; EDX spectra of CASB (c), Pb(II)-loaded CASB (d)

The SEM images of CASB before and after the biosorption process confirmed the physical changes during the biosorption process. SEM image of CASB before (Figure 7.13a) biosorption had some smooth and porous areas on the surface, while CASB after biosorption had a rougher surface (Figure 7.13b). These indicate that the CASB surface was covered by Pb(II) ions after the biosorption process.

This observation was confirmed by EDX analysis before (Figure 7.13c) and after (Figure 7.13d) biosorption. After the Pb(II) removal process the EDX spectrum clearly displayed Pb(II) signals along with the appearance of gold peaks in the spectra. Similar observations have been observed by (Bordoloi et al., 2017).

On the other hand, the intensity of the K^+ signal at between 3 and 4 keV slightly decreased after Pb(II) sorption. This finding supports the existence of an ion–exchange mechanism, which is also predicted by the E value of the D–R isotherm model and may have a role in the biosorption process.

Furthermore, analysis of EDX elementary composition demonstrated that the CASB not only had higher elementary quantities 54.53% carbon and 11.85% oxygen (Data for EDX is given as Wt%), but it also contains some of the amounts of ash elements like 5.93% K, 1.94% P, 0.01% Ca, 1.37% Mg, among others. We can observe Wt% of these elements was changed after the Pb(II) biosorption process to 50.86%, 15.55%, 2.80%, 2.13%, 0.85%, 0.83%, respectively. According to EDX data, there is 4.95% of Pb after the biosorption process, which demonstrated that Pb(II) species was biosorbed onto the CASB surface.

8. CONCLUSIONS AND SUGGESTIONS

Our study reported CASB as a new biochar prepared from CASs as feedstock due to its cost–effective and good biosorption performance for Pb(II). The biosorption properties of Pb(II) ions on CASB were investigated by batch and dynamic flow mode treatments. The effective parameters such as pH, biosorbent amount, initial Pb(II) concentration and contact time were optimized. The maximum monolayer biosorption capacity for Pb(II) by CASB was 36.43 mg g^{-1} under optimized conditions. The biosorption process obeys the Langmuir isotherm model. The pseudo–first–order kinetic model exhibited a better fit for the biosorption data of Pb(II) than the pseudo–second–order kinetic model. In consecutive biosorption-desorption applications, EDTA and HCl were determined as eluents providing 100% desorption. CASB shows excellent Pb(II) removal efficiencies 100% from juice samples spiked with 1.0 mg L^{-1} and 2.5 mg L^{-1} Pb(II). Breakthrough curve analysis indicated that exhausting points of the fixed bed columns packed with CASB were recorded as 320 and 195 min for synthetic Pb(II) solution and SW.

In conclusion, findings of our study showed that CASB has the potential to be used in the treatment of contaminated fruit juices and wastewater treatment applications.

REFERENCES

Abbas, Z., Ali, S., Rizwan, M., Zaheer, I. E., Malik, A., Riaz, M. A., Shahid, M. R., ur Rehman, M. Z., Al-Wabel, M. I., 2018, A critical review of mechanisms involved in the adsorption of organic and inorganic contaminants through biochar, Arabian Journal of Geosciences, 11, 16, 448.

Abdelhadi, S. O., Dosoretz, C. G., Rytwo, G., Gerchman, Y., Azaizeh, H., 2017, Production of biochar from olive mill solid waste for heavy metal removal, Bioresource Technology, 244, 759-767.

Abdelhafez, A. A.,Li, J., 2016, Removal of Pb(II) from aqueous solution by using biochars derived from sugar cane bagasse and orange peel, Journal of the Taiwan Institute of Chemical Engineers, 61, 367-375.

Abu Hasan, H., Sheikh Abdullah, S. R., Tan Kofli, N., Yeoh, S. J., 2016, Interaction of environmental factors on simultaneous biosorption of lead and manganese ions by locally isolated *Bacillus cereus*, Journal of Industrial and Engineering Chemistry, 37, 295-305.

Agarwal, M., Tardio, J., Mohan, S. V., 2015, Pyrolysis biochar from cellulosic municipal solid waste as adsorbent for azo dye removal: equilibrium isotherms and kinetics analysis, International Journal of Environmental Science and Development, 6, 1, 67.

Agwu, K., Okoye, C., Okeji, M., Clifford, E., 2018, Potential Health Impacts of Heavy Metal Concentrations in Fresh and Marine Water Fishes Consumed in Southeast, Nigeria, Pakistan Journal of Nutrition, 17, 12, 647-653.

Ahmad, M., Lee, S. S., Dou, X., Mohan, D., Sung, J.-K., Yang, J. E., Ok, Y. S., 2012, Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water, Bioresource Technology, 118, 536-544.

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S. S., Ok, Y. S., 2014, Biochar as a sorbent for contaminant management in soil and water: A review, Chemosphere, 99, 19-33.

Ahmad, Z., Gao, B., Mosa, A., Yu, H., Yin, X., Bashir, A., Ghoveisi, H., Wang, S., 2018, Removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions by biochars derived from potassium-rich biomass, Journal of Cleaner Production, 180, 437-449.

Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., Chen, M., 2016, Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater, Bioresource Technology, 214, 836-851.

REFERENCES (continued)

Akar, S. T., Aslan, S., Akar, T., 2018, Conversion of natural mineral to effective geosorbent by coating MnO_2 and its application potential for dye contaminated wastewaters, Journal of Cleaner Production, 189, 887-897.

Aksu, Z., 2005, Application of biosorption for the removal of organic pollutants: a review, Process Biochemistry, 40, 3, 997-1026.

Al-Wakeel, K. Z., Abd El Monem, H., Khalil, M. M. H., 2015, Removal of divalent manganese from aqueous solution using glycine modified chitosan resin, Journal of Environmental Chemical Engineering, 3, 1, 179-186.

Al Hawari, A., 2004, Biosorption of Lead, Copper, Cadmium and Nickel by Anaerobic Biomass, Doctor of Philosophy Thesis, Concordia University, Bulding, Civil and Engineering, 192 s.

Alam, M. S., Swaren, L., von Gunten, K., Cossio, M., Bishop, B., Robbins, L. J., Hou, D., Flynn, S. L., Ok, Y. S., Konhauser, K. O., Alessi, D. S., 2018, Application of surface complexation modeling to trace metals uptake by biochar-amended agricultural soils, Applied Geochemistry, 88, 103-112.

Arief, V. O., Trilestari, K., Sunarso, J., Indraswati, N., Ismadji, S., 2008, Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies, CLEAN–Soil, Air, Water, 36, 12, 937-962.

Arslan, D.,Özcan, M. M., 2011, Dehydration of red bell-pepper (*Capsicum annuum* L.): Change in drying behavior, colour and antioxidant content, Food and Bioproducts Processing, 89, 4, 504-513.

Atkinson, B.,Bux F, K. H., 1998, Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents, Water SA,24, 129–135.

Azouaou, N., Sadaoui, Z., Djaafri, A., Mokaddem, H., 2010, Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics, Journal of Hazardous Materials, 184, 1, 126-134.

Baby, R., Saifullah, B., Hussein, M. Z., 2019, Carbon Nanomaterials for the Treatment of Heavy Metal-Contaminated Water and Environmental Remediation, Nanoscale Research Letters, 14, 1, 341.

Bai R, S.,Abraham, T. E., 2001, Biosorption of Cr (VI) from aqueous solution by *Rhizopus nigricans*, Bioresource Technology, 79, 1, 73-81.

REFERENCES (continued)

Bande, R. M., Prasad, B., Mishra, I. M., Wasewar, K. L., 2008, Oil field effluent water treatment for safe disposal by electroflotation, Chemical Engineering Journal, 137, 3, 503-509.

Belala, Z., Jeguirim, M., Belhachemi, M., Addoun, F., Trouvé, G., 2011, Biosorption of basic dye from aqueous solutions by Date Stones and Palm-Trees Waste: Kinetic, equilibrium and thermodynamic studies, Desalination, 271, 1, 80-87.

Bhatnagar, A., 2006, Environmental cardiology Studying mechanistic links between pollution and heart disease, Circulation Research, 99, 7, 692-705.

Bohdziewicz, J.,Sroka, E., 2005, Integrated system of activated sludge–reverse osmosis in the treatment of the wastewater from the meat industry, Process Biochemistry, 40, 5, 1517-1523.

Bordoloi, N., Goswami, R., Kumar, M., Kataki, R., 2017, Biosorption of Co (II) from aqueous solution using algal biochar: kinetics and isotherm studies, Bioresource Technology, 244, 1465-1469.

Bosland, P. W., 1994, Chiles: history, cultivation, and uses, Developments in Food Science.

Bradl, H. B., 2004, Adsorption of heavy metal ions on soils and soils constituents, Journal of Colloid and Interface Science, 277, 1, 1-18.

Brady, J. M.,Tobin, J. M., 1994, Adsorption of metal ions by *Rhizopus arrhizus* biomass: Characterization studies, Enzyme and Microbial Technology, 16, 8, 671-675.

Burch, S., 2018, Evaluating Biochar for the Sustainable Treatment of Heavy Metals in Stormwater: Characteristics, Mechanisms, and Barriers, Doctor of Philosophy Thesis, Oregon State University, 129 s.

Calderon, J., Ortiz-Perez, D., Yanez, L., Diaz-Barriga, F., 2003, Human exposure to metals. Pathways of exposure, biomarkers of effect, and host factors, Ecotoxicology and Environmental Safety, 56, 1, 93.

Canfield, R. L., Henderson Jr, C. R., Cory-Slechta, D. A., Cox, C., Jusko, T. A., Lanphear, B. P., 2003, Intellectual impairment in children with blood lead concentrations below 10 µg per deciliter, The New England Journal of Medicine, 348, 16, 1517-1526.

Cao, X., Ma, L., Gao, B., Harris, W., 2009, Dairy-manure derived biochar effectively sorbs lead and atrazine, Environmental Science & Technology, 43, 9, 3285-3291.

REFERENCES (continued)

Chen, B.-Y., Chen, C.-Y., Guo, W.-Q., Chang, H.-W., Chen, W.-M., Lee, D.-J., Huang, C.-C., Ren, N.-Q., Chang, J.-S., 2014, Fixed-bed biosorption of cadmium using immobilized *Scenedesmus obliquus* CNW-N cells on loofa (*Luffa cylindrica*) sponge, Bioresource Technology, 160, 175-181.

Chen, J., Tong, Y., Xu, J., Liu, X., Li, Y., Tan, M., Li, Y., 2012a, Environmental lead pollution threatens the children living in the Pearl River Delta region, China, Environmental Science and Pollution Research, 19, 8, 3268-3275.

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B., Hay, A. G., 2011, Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution, Bioresource Technology, 102, 19, 8877-8884.

Chen, Z., Chen, B., Chiou, C. T., 2012b, Fast and slow rates of naphthalene sorption to biochars produced at different temperatures, Environmental Science & Technology, 46, 20, 11104-11111.

Chen, Z., Chen, B., Zhou, D., Chen, W., 2012c, Bisolute sorption and thermodynamic behavior of organic pollutants to biomass-derived biochars at two pyrolytic temperatures, Environmental Science & Technology, 46, 22, 12476-12483.

Chen, Z., Xiao, X., Chen, B., Zhu, L., 2015, Quantification of chemical states, dissociation constants and contents of oxygen-containing groups on the surface of biochars produced at different temperatures, Environmental Science & Technology, 49, 1, 309-317.

Chojnacka, K., 2010a, Biosorption and bioaccumulation – the prospects for practical applications, Environment International, 36, 3, 299-307.

Chojnacka, K., 2010b, Biosorption and bioaccumulation in practice, Nova Science Publishers, New York, p.149.

Chowdhury, S., Sikder, J., Mandal, T., Halder, G., 2019, Comprehensive analysis on sorptive uptake of enrofloxacin by activated carbon derived from industrial paper sludge, Science of the Total Environment, 665, 438-452.

Chun, Y., Sheng, G., Chiou, C. T., Xing, B., 2004, Compositions and Sorptive Properties of Crop Residue-Derived Chars, Environmental Science & Technology, 38, 17, 4649-4655.

Chung, H.-K., Kim, W.-H., Park, J., Cho, J., Jeong, T.-Y., Park, P.-K., 2015, Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent, Journal of Industrial and Engineering Chemistry, 28, 241-246.

REFERENCES (continued)

Cohen, M. D., Kargacin, B., Klein, C. B., Costa, M., 1993, Mechanisms of chromium carcinogenicity and toxicity, Critical Reviews in Toxicology, 23, 3, 255-281.

Dai, L., Fan, L., Liu, Y., Ruan, R., Wang, Y., Zhou, Y., Zhao, Y., Yu, Z., 2017, Production of bio-oil and biochar from soapstock via microwave-assisted co-catalytic fast pyrolysis, Bioresource Technology, 225, 1-8.

Dai, Y., Zhang, N., Xing, C., Cui, Q., Sun, Q., 2019, The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: A review, Chemosphere, 223, 12-27.

Davies Jr, F., Puryear, J., Newton, R., Egilla, J., Saraiva Grossi, J., 2002, Mycorrhizal fungi increase chromium uptake by sunflower plants: influence on tissue mineral concentration, growth, and gas exchange, Journal of Plant Nutrition, 25, 11, 2389-2407.

de Caprariis, B., De Filippis, P., Hernandez, A. D., Petrucci, E., Petrullo, A., Scarsella, M., Turchi, M., 2017, Pyrolysis wastewater treatment by adsorption on biochars produced by poplar biomass, Journal of Environmental Management, 197, 231-238.

Dhanarani, S., Viswanathan, E., Piruthiviraj, P., Arivalagan, P., Kaliannan, T., 2016, Comparative study on the biosorption of aluminum by free and immobilized cells of *Bacillus safensis* KTSMBNL 26 isolated from explosive contaminated soil, Journal of the Taiwan Institute of Chemical Engineers, 69, 61-67.

Dhara Shukla,Vankar, P. S., 2015, Biosorption and bioaccumulation of Chromium VI by different fungal species, Fungal Biomolecules: sources, applications and recent developments, 1st edition, V. K. Gupta, R. L. Mach, S. Sreenivasaprasad (Eds.), John Wiley & Sons, p. 333-344.

Ding, W., Dong, X., Ime, I. M., Gao, B., Ma, L. Q., 2014, Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars, Chemosphere, 105, 68-74.

Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, Y., Zheng, B., Cai, X., 2016, Competitive removal of Cd (II) and Pb (II) by biochars produced from water hyacinths: performance and mechanism, Rsc Advances, 6, 7, 5223-5232.

Dizge, N., Keskinler, B., Barlas, H., 2009, Sorption of Ni(II) ions from aqueous solution by Lewatit cation-exchange resin, Journal of Hazardous Materials, 167, 1, 915-926.

Doble, M.,Kumar, A., 2005, Biotreatment of Industrial Effluents, Elsevier.

REFERENCES (continued)

Du, Q., Liu, S., Cao, Z., Wang, Y., 2005, Ammonia removal from aqueous solution using natural Chinese clinoptilolite, Separation and Purification Technology, 44, 3, 229-234.

Du, Z., Zheng, T., Wang, P., Hao, L., Wang, Y., 2016, Fast microwave-assisted preparation of a low-cost and recyclable carboxyl modified lignocellulose-biomass jute fiber for enhanced heavy metal removal from water, Bioresource Technology, 201, 41-49.

Dubinin, M., 1960, The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces, Chemical Reviews, 60, 2, 235-241.

Dubinin, M.,Radushkevich, L., 1947, The equation of the characteristic curve of activated charcoal, 55, 875-890.

Dubinin, M. M., 1965, Modern state of the theory of volume filling of micropore adsorbents during adsorption of gases and steams on carbon adsorbents, Zhurnal Fizicheskoi Khimii, 39, 19, 1305-1317.

Duffus, J. H.,Worth, H. G., 1996, Fundamental toxicology for chemists, Royal Society of Chemistry, p.285.

Duku, M. H., Gu, S., Hagan, E. B., 2011, Biochar production potential in Ghana—A review, Renewable and Sustainable Energy Reviews, 15, 8, 3539-3551.

Duran-Jimenez, G., Monti, T., Titman, J. J., Hernandez-Montoya, V., Kingman, S. W., Binner, E. R., 2017, New insights into microwave pyrolysis of biomass: Preparation of carbon-based products from pecan nutshells and their application in wastewater treatment, Journal of Analytical and Applied Pyrolysis, 124, 113-121.

El-Adawy, T. A.,Taha, K. M., 2001, Characteristics and composition of watermelon, pumpkin, and paprika seed oils and flours, Journal of Agricultural and Food Chemistry, 49, 3, 1253-1259.

El-Safty, A., Metwaly, F., Rashd, H., Bayoumi, F., 2009, Susceptibility to Infection among Nickel electroplaters, Journal of American Science, 5, 74-82.

Elkhalifa, S., Al-Ansari, T., Mackey, H. R., McKay, G., 2019, Food waste to biochars through pyrolysis: A review, Resources, Conservation & Recycling, 144, 310-320.

EPA (2000). Wastewater Technology Fact Sheet Chemical Precipitation. Washington, DC**:** 1-8.

Esmaeili, A.,Beni, A. A., 2014, A novel fixed-bed reactor design incorporating an electrospun PVA/chitosan nanofiber membrane, Journal of Hazardous Materials, 280, 788-796.

REFERENCES (continued)

Esposito, A., Pagnanelli, F., Vegliò, F., 2002, pH-related equilibria models for biosorption in single metal systems, Chemical Engineering Science, 57, 3, 307-313.

Farcasanu, I. C., Popa, C. V., Ruta, L. L., 2018, Calcium and Cell Response to Heavy Metals: Can Yeast Provide an Answer?, Calcium and Signal Transduction, J. N. Buchholz (Ed.), BoD–Books on Demand, p.

Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y.-H., Indraswati, N., Ismadji, S., 2009, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, Journal of Hazardous Materials, 162, 2, 616-645.

Feizi, M.,Jalali, M., 2015, Removal of heavy metals from aqueous solutions using sunflower, potato, canola and walnut shell residues, Journal of the Taiwan Institute of Chemical Engineers, 54, 125-136.

Fierro, V., Torné-Fernández, V., Montané, D., Celzard, A., 2008, Adsorption of phenol onto activated carbons having different textural and surface properties, Microporous and Mesoporous Materials, 111, 1, 276-284.

Flegal, A. R.,Smith, D. R., 1992, Current needs for increased accuracy and precision in measurements of low levels of lead in blood, Environmental Research, 58, 1, 125-133.

Fomina, M.,Gadd, G. M., 2014, Biosorption: current perspectives on concept, definition and application, Bioresource Technology, 160, 3-14.

Fourest, E.,Roux, J.-C., 1992, Heavy metal biosorption by fungal mycelial by-products: mechanisms and influence of pH, Applied Microbiology and Biotechnology, 37, 3, 399-403.

Freundlich, H. M. F., 1906, Over the adsorption in solution, Journal of Physical Chemistry, 57, 385471, 1100-1107.

Gadd, G. M., 1992, Metals and microorganisms: a problem of definition, FEMS Microbiology Letters, 100, 1-3, 197-203.

Gadd, G. M.,Gadd, G., 1988, Accumulation of metals by microorganisms and algae, Biotechnology. Vol. 6b, Special Microbial Processes, H.-J. Rehm, G. Reed (Eds.), VCH Verlagesellschaft, p. 401-433.

García-Lestón, J., Méndez, J., Pásaro, E., Laffon, B., 2010, Genotoxic effects of lead: An updated review, Environment International, 36, 6, 623-636.

REFERENCES (continued)

Gell, K., van Groenigen, J., Cayuela, M. L., 2011, Residues of bioenergy production chains as soil amendments: Immediate and temporal phytotoxicity, Journal of Hazardous Materials, 186, 2, 2017-2025.

Gode, F.,Pehlivan, E., 2007, Sorption of Cr(III) onto chelating b-DAEG–sporopollenin and CEP–sporopollenin resins, Bioresource Technology, 98, 4, 904-911.

Golie, W. M.,Upadhyayula, S., 2017, An investigation on biosorption of nitrate from water by chitosan based organic-inorganic hybrid biocomposites, International Journal of Biological Macromolecules, 97, 489-502.

Gomez-Gonzalez, R., Cerino-Córdova, F. J., Garcia-León, A. M., Soto-Regalado, E., Davila-Guzman, N. E., Salazar-Rabago, J. J., 2016, Lead biosorption onto coffee grounds: Comparative analysis of several optimization techniques using equilibrium adsorption models and ANN, Journal of the Taiwan Institute of Chemical Engineers, 68, 201-210.

Gopinath, A., Krishna, K., Karthik, C., 2020, Adsorptive removal and recovery of heavy metal ions from aqueous solution/effluents using conventional and non-conventional materials, Modern age waste water problems, Mohammad Oves, Mohammad Omaish Ansari, Mohammad Zain Khan, Mohammad Shahadat, I. M. I. Ismail (Eds.), Springer, p. 309-328.

Gunatilake, S., 2015, Methods of removing heavy metals from industrial wastewater, Journal of Multidisciplinary Engineering Science Studies, 1, 1, 14.

Gupta, V. K.,Ali, I., 2012, Environmental Water: Advances in Treatment, Remediation and Recycling, 1st Edition, Elsevier Science, Amsterdam, Netherlands, p.216.

Hall, K. R., Eagleton, L. C., Acrivos, A., Vermeulen, T., 1966, Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, Industrial & Engineering Chemistry Fundamentals, 5, 2, 212-223.

Hamdaoui, O., 2009, Removal of copper(II) from aqueous phase by Purolite C100-MB cation exchange resin in fixed bed columns: Modeling, Journal of Hazardous Materials, 161, 2, 737-746.

Han, R., Zhang, J., Zou, W., Shi, J., Liu, H., 2005, Equilibrium biosorption isotherm for lead ion on chaff, Journal of Hazardous Materials, 125, 1, 266-271.

Han, Y., Cao, X., Ouyang, X., Sohi, S. P., Chen, J., 2016, Adsorption kinetics of magnetic biochar derived from peanut hull on removal of Cr (VI) from aqueous solution: Effects of production conditions and particle size, Chemosphere, 145, 336-341.

REFERENCES (continued)

Harvey, O. R., Herbert, B. E., Rhue, R. D., Kuo, L.-J., 2011, Metal interactions at the biochar-water interface: energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry, Environmental Science & Technology, 45, 13, 5550-5556.

Hayes, K. F., 1987, Equilibrium, spectroscopic, and kinetic studies of ion adsorption at the oxide-aqueous interface, Doctor of Philosophy Thesis, Stanford University, s.

He, B., Yun, Z., Shi, J., Jiang, G., 2013, Research progress of heavy metal pollution in China: sources, analytical methods, status, and toxicity, Chinese Science Bulletin, 58, 2, 134-140.

He, J.,Chen, J. P., 2014, A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry, and modeling simulation tools, Bioresource Technology, 160, 67-78.

Heidari, A., Stahl, R., Younesi, H., Rashidi, A., Troeger, N., Ghoreyshi, A. A., 2014, Effect of process conditions on product yield and composition of fast pyrolysis of *Eucalyptus grandis* in fluidized bed reactor, Journal of Industrial and Engineering Chemistry, 20, 4, 2594-2602.

Helby, W. A., 1952, Adsorption isotherm studies, Chemical Engineering Journal, 59, 153-158.

Helfferich, F., 1962, Ion Exchange, McGraw-Hill, New York.

Higashikawa, F. S., Conz, R. F., Colzato, M., Cerri, C. E. P., Alleoni, L. R. F., 2016, Effects of feedstock type and slow pyrolysis temperature in the production of biochars on the removal of cadmium and nickel from water, Journal of Cleaner Production, 137, 965-972.

Hlihor, R. M., Diaconu, M., Leon, F., Curteanu, S., Tavares, T., Gavrilescu, M., 2015, Experimental analysis and mathematical prediction of Cd(II) removal by biosorption using support vector machines and genetic algorithms, New Biotechnology, 32, 3, 358-368.

Ho, S.-H., Chen, Y.-d., Yang, Z.-k., Nagarajan, D., Chang, J.-S., Ren, N.-q., 2017, High-efficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge, Bioresource Technology, 246, 142-149.

Ho, Y. S.,McKay, G., 1999, Pseudo-second order model for sorption processes, Process Biochemistry, 34, 5, 451-465.

Ho, Y. S.,McKay, G., 2003, Sorption of dyes and copper ions onto biosorbents, Process Biochemistry, 38, 7, 1047-1061.

REFERENCES (continued)

Hobson, J. P., 1969, Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure, The Journal of Physical Chemistry, 73, 8, 2720-2727.

Hossain, A., Bhattacharyya, S. R., Aditya, G., 2015, Biosorption of cadmium from aqueous solution by shell dust of the freshwater snail *Lymnaea luteola*, Environmental Technology & Innovation, 4, 82-91.

Hu, X., Xu, J., Wu, M., Xing, J., Bi, W., Wang, K., Ma, J., Liu, X. e., 2017, Effects of biomass pre-pyrolysis and pyrolysis temperature on magnetic biochar properties, Journal of Analytical and Applied Pyrolysis, 127, 196-202.

Huang, C.-p., Huang, C.-p., Morehart, A. L., 1990, The removal of Cu(II) from dilute aqueous solutions by *Saccharomyces cerevisiae*, Water Research, 24, 4, 433-439.

Hyder, O., Chung, M., Cosgrove, D., Herman, J. M., Li, Z., Firoozmand, A., Gurakar, A., Koteish, A., Pawlik, T. M., 2013, Cadmium exposure and liver disease among US adults, Journal of Gastrointestinal Surgery, 17, 7, 1265-1273.

Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A. R., Cao, X., 2011, Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse, Separation Science and Technology, 46, 12, 1950-1956.

Inyang, M. I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y. S., Cao, X., 2016, A review of biochar as a low-cost adsorbent for aqueous heavy metal removal, Critical Reviews in Environmental Science and Technology, 46, 4, 406-433.

Isidoro, E., Cotter, D. J., Fernandez, G. C., Southward, G. M., 1995, Color retention in red chile powder as related to delayed harvest, Journal of Food Science, 60, 5, 1075-1077.

J Binkley,Simpson, J. A., 2003, Microbiology of wastewater treatment, Handbook of Water and Wastewater Microbiology, Duncan Mara, N. J. Horan (Eds.), Elsevier, Academic Press, p. 317-610.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., Beeregowda, K. N., 2014, Toxicity, mechanism and health effects of some heavy metals, Interdisciplinary Toxicology, 7, 2, 60-72.

James, A., 2001, The Treatment of Toxic Wastes, Pollution Causes, Effects and Control, R. M. Harrison (Ed.), Cambridge: Royal Society of Chemistry, p. 145-168.

REFERENCES (continued)

Jaramillo, J., Gómez-Serrano, V., Álvarez, P. M., 2009, Enhanced adsorption of metal ions onto functionalized granular activated carbons prepared from cherry stones, Journal of Hazardous Materials, 161, 2, 670-676.

Järup, L., 2003, Hazards of heavy metal contamination, British Medical Bulletin, 68, 1, 167-182.

Jeon, C.,Höll, W. H., 2004, Application of the surface complexation model to heavy metal sorption equilibria onto aminated chitosan, Hydrometallurgy, 71, 3, 421-428.

Jeong, Y. W., Choi, S. K., Choi, Y. S., Kim, S. J., 2015, Production of biocrude-oil from swine manure by fast pyrolysis and analysis of its characteristics, Renewable Energy, 79, 14-19.

Jes´us S´anchez-Mart´ın,Beltr´an-Heredia, J. u., 2012, Nature Is the Answer: Water and Wastewater Treatment by New Natural-Based Agents, Advances in Water Treatment and Pollution Prevention, S. K. Sharma, R. Sanghi (Eds.), Springer, p. 337-376.

Jia, M., Wang, F., Bian, Y., Jin, X., Song, Y., Kengara, F. O., Xu, R., Jiang, X., 2013, Effects of pH and metal ions on oxytetracycline sorption to maize-straw-derived biochar, Bioresource Technology, 136, 87-93.

Jiang, T.-Y., Jiang, J., Xu, R.-K., Li, Z., 2012, Adsorption of Pb(II) on variable charge soils amended with rice-straw derived biochar, Chemosphere, 89, 3, 249-256.

Jindo, K., Mizumoto, H., Sawada, Y., Sánchez-Monedero, M. Á., Sonoki, T., 2014, Physical and chemical characterization of biochars derived from different agricultural residues, Biogeosciences.

Jinsheng Sun, Yulan Ji, Fang Cai, Li, J., 2012, Heavy Metal Removal Through Biosorptive Pathways, Advances in Water Treatment and Pollution Prevention, S. K. Sharma, R. Sanghi (Eds.), Springer, p. 95-145.

Jung, K. W., Jeong, T. U., Choi, B. H., Jeong Kang, H., Ahn, K. H., 2017, Phosphate adsorption from aqueous solution by *Laminaria japonica*-derived biochar-calcium alginate beads in a fixed-bed column: Experiments and prediction of breakthrough curves, Environmental Progress & Sustainable Energy, 36, 5, 1365-1373.

Jüttner, K., Galla, U., Schmieder, H., 2000, Electrochemical approaches to environmental problems in the process industry, Electrochimica Acta, 45, 15, 2575-2594.

Kadali, V. K., 2013, Study of Heavy Metal Biosorption from Water Using a Low-cost Biosorbent: Grapefruit Peel, Thesis, Lamar University, s.

REFERENCES (continued)

Kadimpati, K. K., 2017, Design of hybrid PVA–CA–Jania rubens biomatrix for removal of lead, International Journal of Phytoremediation, 19, 2, 183-190.

Kamarudzaman, A. N., Chay, T. C., Amir, A., Talib, S. A., 2015, Biosorption of Mn(II) ions from Aqueous Solution by *Pleurotus* Spent Mushroom Compost in a Fixed-Bed Column, Procedia- Social and Behavioral Sciences, 195, 2709-2716.

Kambo, H. S.,Dutta, A., 2015, A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications, Renewable and Sustainable Energy Reviews, 45, 359-378.

Kapoor, A.,Viraraghavan, T., 1995, Fungal biosorption — an alternative treatment option for heavy metal bearing wastewaters: a review, Bioresource Technology, 53, 3, 195-206.

Kargi, F.,Özmıhçı, S., 2002, Performance of azotobacter supplemented activated sludge in biological treatment of nitrogen deficient wastewater, Process Biochemistry, 38, 1, 57-64.

Kavitha, B., Reddy, P. V. L., Kim, B., Lee, S. S., Pandey, S. K., Kim, K.-H., 2018, Benefits and limitations of biochar amendment in agricultural soils: A review, Journal of Environmental Management, 227, 146-154.

Khare, P., Dilshad, U., Rout, P. K., Yadav, V., Jain, S., 2017, Plant refuses driven biochar: Application as metal adsorbent from acidic solutions, Arabian Journal of Chemistry, 10, S3054-S3063.

Kılıç, M., Kırbıyık, Ç., Çepelioğullar, Ö., Pütün, A. E., 2013, Adsorption of heavy metal ions from aqueous solutions by bio-char, a by-product of pyrolysis, Applied Surface Science, 283, 856-862.

Kim, W.-K., Shim, T., Kim, Y.-S., Hyun, S., Ryu, C., Park, Y.-K., Jung, J., 2013, Characterization of cadmium removal from aqueous solution by biochar produced from a giant *Miscanthus* at different pyrolytic temperatures, Bioresource Technology, 138, 266-270.

Kizito, S., Wu, S., Wandera, S. M., Guo, L., Dong, R., 2016, Evaluation of ammonium adsorption in biochar-fixed beds for treatment of anaerobically digested swine slurry: Experimental optimization and modeling, Science of the Total Environment, 563-564, 1095-1104.

Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M. H., Soja, G., 2012, Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties, Journal of Environmental Quality, 41, 4, 990-1000.

REFERENCES (continued)

Komkiene, J.,Baltrenaite, E., 2016, Biochar as adsorbent for removal of heavy metal ions [Cadmium(II), Copper(II), Lead(II), Zinc(II)] from aqueous phase, International Journal of Environmental Science and Technology, 13, 2, 471-482.

Korkutata, N. F.,Kavaz, A., 2015, A comparative study of ascorbic acid and capsaicinoid contents in red hot peppers (*Capsicum annum* L.) grown in southeastern Anatolia region, International Journal of Food Properties, 18, 4, 725-734.

Kotrba, P., 2011, Microbial Biosorption of Metals—General Introduction, Microbial biosorption of metals, Pavel Kotrba, Martina Mackova, T. Macek (Eds.), Springer, p. 1-6.

Kumar, P., Singh, H., Kapur, M., Mondal, M. K., 2014, Comparative study of malathion removal from aqueous solution by agricultural and commercial adsorbents, Journal of Water Process Engineering, 3, 67-73.

Kumar, R., Mishra, R. K., Mishra, V., Qidwai, A., Pandey, A., Shukla, S. K., Pandey, M., Pathak, A., Dikshit, A., 2016, Detoxification and Tolerance of Heavy Metals in Plants, Plant Metal Interaction, P. Ahmad (Ed.), Elsevier, p. 335-359.

Lagergren, S. K., 1898, About the theory of so-called adsorption of soluble substances, Sven. Vetenskapsakad. Handingarl, 24, 1-39.

Langmuir, I., 1916, The constitution and fundamental properties of solids and liquids. Part I. Solids, Journal of the American Chemical Society, 38, 11, 2221-2295.

Larry D. Benefield,Morgan, J. M., 1999, Chemical Precipitation, Water quality and treatment A Handbook of Community Water Supplies, 5th Edition, R. D. Letterman (Ed.), New York, McGraw-Hill, p. 10.11-10.57.

Lee, E. H., Park, R.-s., Kim, H., Park, S. H., Jung, S.-C., Jeon, J.-K., Kim, S. C., Park, Y.-K., 2016, Hydrodeoxygenation of guaiacol over Pt loaded zeolitic materials, Journal of Industrial and Engineering Chemistry, 37, 18-21.

Lee, J., Lee, K., Sohn, D., Kim, Y. M., Park, K. Y., 2018, Hydrothermal carbonization of lipid extracted algae for hydrochar production and feasibility of using hydrochar as a solid fuel, Energy, 153, 913-920.

Lee, S.-J., Park, J. H., Ahn, Y.-T., Chung, J. W., 2015, Comparison of heavy metal adsorption by peat moss and peat moss-derived biochar produced under different carbonization conditions, Water, Air, & Soil Pollution, 226, 2, 9.

REFERENCES (continued)

Lehmann, J.,Joseph, S., 2015, Biochar for environmental management: An introduction, Biochar for environmental management: science and technology, Johannes Lehmann, S. Joseph (Eds.), London, UK, Routledge, p. 1-12.

Li, B., Yang, L., Wang, C.-q., Zhang, Q.-p., Liu, Q.-c., Li, Y.-d., Xiao, R., 2017, Adsorption of Cd(II) from aqueous solutions by rape straw biochar derived from different modification processes, Chemosphere, 175, 332-340.

Li, H., Zhang, Z., Wang, H., Xu, X., Lin, Y., Zhang, J., Jun, Z., 2011, Biological phosphorus removal performance and relevant microorganism characteristics of activated sludge in municipal wastewater treatment plants, China, Water Environment Research, 83, 7, 594-602.

Li, M., Liu, Q., Guo, L., Zhang, Y., Lou, Z., Wang, Y., Qian, G., 2013, Cu(II) removal from aqueous solution by *Spartina alterniflora* derived biochar, Bioresource Technology, 141, 83-88.

Li, X., Ming, Q., Cai, R., Yue, T., Yuan, Y., Gao, Z., Wang, Z., 2020, Biosorption of Cd2+ and Pb2+ from apple juice by the magnetic nanoparticles functionalized lactic acid bacteria cells, Food Control, 109, 106916.

Li, Z., Ma, Z., van der Kuijp, T. J., Yuan, Z., Huang, L., 2014, A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment, Science of the Total Environment, 468-469, 843-853.

Liang, J., Li, X., Yu, Z., Zeng, G., Luo, Y., Jiang, L., Yang, Z., Qian, Y., Wu, H., 2017, Amorphous MnO2 modified biochar derived from aerobically composted swine manure for adsorption of Pb (II) and Cd (II), ACS Sustainable Chemistry & Engineering, 5, 6, 5049-5058.

Libra, J. A., Ro, K. S., Kammann, C., Funke, A., Berge, N. D., Neubauer, Y., Titirici, M.-M., Fühner, C., Bens, O., Kern, J., 2011, Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, Biofuels, 2, 1, 71-106.

Lima, I. M., Boateng, A. A., Klasson, K. T., 2010, Physicochemical and adsorptive properties of fast-pyrolysis bio-chars and their steam activated counterparts, Journal of Chemical Technology & Biotechnology, 85, 11, 1515-1521.

Liu, J., Huang, Z., Chen, Z., Sun, J., Gao, Y., Wu, E., 2020, Resource utilization of swine sludge to prepare modified biochar adsorbent for the efficient removal of Pb(II) from water, Journal of Cleaner Production, 257, 120322.

REFERENCES (continued)

Liu, X., Li, Z., Zhang, Y., Feng, R., Mahmood, I. B., 2014, Characterization of human manure-derived biochar and energy-balance analysis of slow pyrolysis process, Waste Management, 34, 9, 1619-1626.

Liu, Y.,Liu, Y.-J., 2008, Biosorption isotherms, kinetics and thermodynamics, Separation and Purification Technology, 61, 3, 229-242.

Liu, Y.,Wang, J., 2009, Fundamentals and applications of biosorption isotherms, kinetics and thermodynamics, Nova Science Publishers, New York, United States.

Liu, Z.,Han, G., 2015, Production of solid fuel biochar from waste biomass by low temperature pyrolysis, Fuel, 158, 159-165.

Liu, Z.,Zhang, F.-S., 2009, Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass, Journal of Hazardous Materials, 167, 1, 933-939.

Liu, Z., Zhang, F.-S., Wu, J., 2010, Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment, Fuel, 89, 2, 510-514.

Lodeiro, P., Herrero, R., de Vicente, M. E. S., 2006, Thermodynamic and kinetic aspects on the biosorption of cadmium by low cost materials: a review, Environmental Chemistry, 3, 6, 400-418.

Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R., 2012, Relative distribution of Pb^{2+} sorption mechanisms by sludge-derived biochar, Water Research, 46, 3, 854-862.

Lü, J., Li, J., Li, Y., Chen, B., Bao, Z., 2012, Use of rice straw biochar simultaneously as the sustained release carrier of herbicides and soil amendment for their reduced leaching, Journal of Agricultural and Food Chemistry, 60, 26, 6463-6470.

Lucaci, A. R., Bulgariu, D., Popescu, M.-C., Bulgariu, L., 2020, Adsorption of Cu (II) Ions on Adsorbent Materials Obtained from Marine Red Algae Callithamnion corymbosum sp, Water, 12, 2, 372.

Luning, P. A., Yuksel, D., Van Der Vuurst De Vries, R. I. A., Roozen, J. P., 1995, Aroma changes in fresh bell peppers (*Capsicum annuum*) after hot-air drying, Journal of Food Science, 60, 6, 1269-1276.

Luque, R., Menendez, J. A., Arenillas, A., Cot, J., 2012, Microwave-assisted pyrolysis of biomass feedstocks: the way forward?, Energy & Environmental Science, 5, 2, 5481-5488.

REFERENCES (continued)

Mahdi, Z., Yu, Q. J., El Hanandeh, A., 2018, Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar, Journal of Environmental Chemical Engineering, 6, 1, 1171-1181.

Malakootian, M., Khodashenas Limoni, Z., Malakootian, M., 2016, The efficiency of lead biosorption from industrial wastewater by micro-alga spirulina platensis, International Journal of Environmental Research, 10, 3, 357-366.

Malik, A., 2004, Metal bioremediation through growing cells, Environment International, 30, 2, 261-278.

Mara dos Santos Barbosa, J., Ré-Poppi, N., Santiago-Silva, M., 2006, Polycyclic aromatic hydrocarbons from wood pyrolyis in charcoal production furnaces, Environmental Research, 101, 3, 304-311.

Meikle, A. J., Gadd, G. M., Reed, R. H., 1990, Manipulation of yeast for transport studies: Critical assessment of cultural and experimental procedures, Enzyme and Microbial Technology, 12, 11, 865-872.

Meyer, S., Glaser, B., Quicker, P., 2011, Technical, economical, and climate-related aspects of biochar production technologies: a literature review, Environmental Science & Technology, 45, 22, 9473-9483.

Michalak, I., Chojnacka, K., Witek-Krowiak, A., 2013, State of the art for the biosorption process—a review, Applied Biochemistry and Biotechnology, 170, 6, 1389-1416.

Mohan, D., Pittman, C. U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P. H., Alexandre-Franco, M. F., Gómez-Serrano, V., Gong, H., 2007, Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, Journal of Colloid and Interface Science, 310, 1, 57-73.

Mohan, D., Sarswat, A., Ok, Y. S., Pittman, C. U., 2014, Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review, Bioresource Technology, 160, 191-202.

Mondal, S., Aikat, K., Halder, G., 2016, Ranitidine hydrochloride sorption onto superheated steam activated biochar derived from mung bean husk in fixed bed column, Journal of Environmental Chemical Engineering, 4, 1, 488-497.

Morosanu, I., Teodosiu, C., Paduraru, C., Ibanescu, D., Tofan, L., 2017, Biosorption of lead ions from aqueous effluents by rapeseed biomass, New Biotechnology, 39, 110-124.

REFERENCES (continued)

Mosa, A. A., El-Ghamry, A., Al-Zahrani, H., Selim, E.-M., El-Khateeb, A., 2017, Chemically modified biochar derived from cotton stalks: characterization and assessing its potential for heavy metals removal from wastewater, Environment, Biodiversity and Soil Security, 1, 2017, 33-45.

Mukke, V.,Chinte, D., 2012, Impact of heavy metal induced alterations in Lipase activity of fresh water crab, Barytelphusa guerini, Journal of Chemical and Pharmaceutical Research, 4, 5, 2763-2766.

Mustafa, A. A., 2018, Oxidative Stability of the Red Pepper Seed Oil, Master Thesis, Kahramanmaraş Sütçü İmam University, Department of Bioengineering and Sciences, 56 s.

Nadeem, R., Hanif, M. A., Shaheen, F., Perveen, S., Zafar, M. N., Iqbal, T., 2008, Physical and chemical modification of distillery sludge for Pb(II) biosorption, Journal of Hazardous Materials, 150, 2, 335-342.

Naja, G.,Volesky, B., 2011, The Mechanism of Metal Cation and Anion Biosorption, Microbial Biosorption of Metals, Pavel Kotrba, Martina Mackova, T. Macek (Eds.), p. 19-58.

Niu, H., Xu, X. S., Wang, J. H., Volesky, B., 1993, Removal of lead from aqueous solutions by *Penicillium* biomass, Biotechnology and Bioengineering, 42, 6, 785-787.

Nourbakhsh, M., Sağ, Y., Özer, D., Aksu, Z., Kutsal, T., Çağlar, A., 1994, A comparative study of various biosorbents for removal of chromium(VI) ions from industrial waste waters, Process Biochemistry, 29, 1, 1-5.

NRC, 1980, Lead in the human environment, National Academy of Sciences Washington, DC, National Research Council, p.525.

Oliveira, F. R., Patel, A. K., Jaisi, D. P., Adhikari, S., Lu, H., Khanal, S. K., 2017, Environmental application of biochar: Current status and perspectives, Bioresource Technology, 246, 110-122.

Omolo, M. A., Wong, Z.-Z., Mergen, K., Hastings, J. C., Le, N. C., Reil, H. A., Case, K. A., Baumler, D. J., 2014, Antimicrobial properties of chili peppers, Journal of Infectious Diseases and Therapy.

Onyango, M. S., Kojima, Y., Aoyi, O., Bernardo, E. C., Matsuda, H., 2004, Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, Journal of Colloid and Interface Science, 279, 2, 341-350.

REFERENCES (continued)

Oves, M., Khan, M. S., Zaidi, A., 2013, Chromium reducing and plant growth promoting novel strain *Pseudomonas aeruginosa* OSG41 enhance chickpea growth in chromium amended soils, European Journal of Soil Biology, 56, 72-83.

Özcan, A. S., Özcan, A., Tunali, S., Akar, T., Kiran, I., Gedikbey, T., 2007, Adsorption potential of lead (II) ions from aqueous solutions onto *Capsicum annuum* seeds, Separation Science and Technology, 42, 1, 137-151.

Pagnanelli, F., 2011, Equilibrium, Kinetic and Dynamic Modelling of Biosorption Processes, Microbial Biosorption of Metals, Pavel Kotrba, Martina Mackova, T. Macek (Eds.), Netherlands, Springer, p. 59-120.

Pan, J., Jiang, J., Xu, R., 2013, Adsorption of Cr(III) from acidic solutions by crop straw derived biochars, Journal of Environmental Sciences, 25, 10, 1957-1965.

Parab, H., Joshi, S., Sudersanan, M., Shenoy, N., Lali, A., Sarma, U., 2010, Removal and recovery of cobalt from aqueous solutions by adsorption using low cost lignocellulosic biomass—coir pith, Journal of Environmental Science and Health Part A, 45, 5, 603-611.

Park, D., Yun, Y.-S., Park, J. M., 2010, The past, present, and future trends of biosorption, Biotechnology and Bioprocess Engineering, 15, 1, 86-102.

Park, J.-H., Eom, J.-H., Lee, S.-L., Hwang, S.-W., Kim, S.-H., Kang, S.-W., Yun, J.-J., Cho, J.-S., Lee, Y.-H., Seo, D.-C., 2020, Exploration of the potential capacity of fly ash and bottom ash derived from wood pellet-based thermal power plant for heavy metal removal, Science of the Total Environment, 740, 140205.

Park, J.-H., Ok, Y. S., Kim, S.-H., Cho, J.-S., Heo, J.-S., Delaune, R. D., Seo, D.-C., 2016, Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions, Chemosphere, 142, 77-83.

Park, J. H., Ok, Y. S., Kim, S. H., Kang, S. W., Cho, J. S., Heo, J. S., Delaune, R. D., Seo, D. C., 2015, Characteristics of biochars derived from fruit tree pruning wastes and their effects on lead adsorption, Journal of the Korean Society for Applied Biological Chemistry, 58, 5, 751-760.

Peakall, D.,Burger, J., 2003, Methodologies for assessing exposure to metals: speciation, bioavailability of metals, and ecological host factors, Ecotoxicology and Environmental Safety, 56, 1, 110-121.

REFERENCES (continued)

Poyrazoğlu, E. S., Yemiş, O., Kadakal, Ç., Artık, N., 2005, Determination of capsaicinoid profile of different chilli peppers grown in Turkey, Journal of the Science of Food and Agriculture, 85, 9, 1435-1438.

Puranik, P. R.,Paknikar, K. M., 1997, Biosorption of lead and zinc from solutions using *Streptoverticillium cinnamoneum* waste biomass, Journal of Biotechnology, 55, 2, 113-124.

Qian, K., Kumar, A., Zhang, H., Bellmer, D., Huhnke, R., 2015, Recent advances in utilization of biochar, Renewable and Sustainable Energy Reviews, 42, 1055-1064.

Qian, L.,Chen, B., 2013, Dual role of biochars as adsorbents for aluminum: the effects of oxygen-containing organic components and the scattering of silicate particles, Environmental Science & Technology, 47, 15, 8759-8768.

Radushkevich, L. V., 1949, Potential theory of sorption and structure of carbons, Zhurnal Fizicheskoi Khimii, 23, 12, 1410-1420.

Rangabhashiyam, S., Anu, N., Giri Nandagopal, M. S., Selvaraju, N., 2014, Relevance of isotherm models in biosorption of pollutants by agricultural byproducts, Journal of Environmental Chemical Engineering, 2, 1, 398-414.

Rehman, K., Fatima, F., Waheed, I., Akash, M. S. H., 2018, Prevalence of exposure of heavy metals and their impact on health consequences, Journal of Cellular Biochemistry, 119, 1, 157-184.

Reichenberg, D., 1953, Properties of ion-exchange resins in relation to their structure. III. Kinetics of exchange, Journal of the American Chemical Society, 75, 3, 589-597.

Renu, M. A. a. K. S., 2017, Methodologies for removal of heavy metal ions from wastewater: an overview, Interdisciplinary Environmental Review, 18.

Rosales, E., Meijide, J., Pazos, M., Sanromán, M. A., 2017, Challenges and recent advances in biochar as low-cost biosorbent: from batch assays to continuous-flow systems, Bioresource Technology, 246, 176-192.

Rouquerol, J., Rouquerol, F., Llewellyn, P., Maurin, G., Sing, K. S. W., 2014, Adsorption by powders and porous solids: principles, methodology and applications, 2nd edition, Elsevier, Academic press, p.646.

Russell, S. H., Turrion-Gomez, J. L., Meredith, W., Langston, P., Snape, C. E., 2017, Increased charcoal yield and production of lighter oils from the slow pyrolysis of biomass, Journal of Analytical and Applied Pyrolysis, 124, 536-541.

REFERENCES (continued)

Rusyniak, D. E., Arroyo, A., Acciani, J., Froberg, B., Kao, L., Furbee, B., 2010, Heavy metal poisoning: management of intoxication and antidotes, Molecular, Clinical and Environmental Toxicology, A. Luch (Ed.), Springer, p. 365-396.

Saeed, A., Akhter, M. W., Iqbal, M., 2005a, Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, Separation and Purification Technology, 45, 1, 25-31.

Saeed, A., Iqbal, M., Akhtar, M. W., 2005b, Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk), Journal of Hazardous Materials, 117, 1, 65-73.

Sağ, Y., Ataçoğlu, I., Kutsal, T., 2000, Equilibrium parameters for the single- and multicomponent biosorption of Cr(VI) and Fe(III) ions on *R. arrhizus* in a packed column, Hydrometallurgy, 55, 2, 165-179.

Saleh, M. E., El-Refaey, A. A., Mahmoud, A. H., 2016, Effectiveness of sunflower seed husk biochar for removing copper ions from wastewater: a comparative study, Soil and Water Research, 11, 1, 53-63.

Sarı, A.,Tuzen, M., 2008, Biosorption of cadmium(II) from aqueous solution by red algae (*Ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies, Journal of Hazardous Materials, 157, 2, 448-454.

Saucier, C., Adebayo, M. A., Lima, E. C., Cataluña, R., Thue, P. S., Prola, L. D. T., Puchana-Rosero, M. J., Machado, F. M., Pavan, F. A., Dotto, G. L., 2015, Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents, Journal of Hazardous Materials, 289, 18-27.

Say, R., Denizli, A., Yakup Arıca, M., 2001, Biosorption of cadmium(II), lead(II) and copper(II) with the filamentous fungus *Phanerochaete chrysosporium*, Bioresource Technology, 76, 1, 67-70.

Schindler, P. W., Fürst, B., Dick, R., Wolf, P. U., 1976, Ligand properties of surface silanol groups. I. surface complex formation with Fe^{3+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}, Journal of Colloid and Interface Science, 55, 2, 469-475.

Shafaghat, H., Rezaei, P. S., Daud, W. M. A. W., 2016, Catalytic hydrodeoxygenation of simulated phenolic bio-oil to cycloalkanes and aromatic hydrocarbons over bifunctional metal/acid catalysts of Ni/HBeta, Fe/HBeta and NiFe/HBeta, Journal of Industrial and Engineering Chemistry, 35, 268-276.

REFERENCES (continued)

Shakoori, A., Makhdoom, M., Haq, R., 2000, Hexavalent chromium reduction by a dichromate-resistant gram-positive bacterium isolated from effluents of tanneries, Applied Microbiology and Biotechnology, 53, 3, 348-351.

Shen, Y., Li, H., Zhu, W., Ho, S.-H., Yuan, W., Chen, J., Xie, Y., 2017, Microalgal-biochar immobilized complex: a novel efficient biosorbent for cadmium removal from aqueous solution, Bioresource Technology, 244, 1031-1038.

Sohi, S., Loez-Capel, E., Krull, E., Bol, R., 2009, Biochar's roles in soil and climate change: A review of research needs, CSIRO Land and Water Science Report, 5, 09, 1-57.

Srinivas, T. R., 2008, Environmental Biotechnology, New Age International Publishers, p.130.

Stöhr, C., Horst, J., Höll, W. H., 2001, Application of the surface complex formation model to ion exchange equilibria: Part V. Adsorption of heavy metal salts onto weakly basic anion exchangers, Reactive and Functional Polymers, 49, 2, 117-132.

Sun, J., Lian, F., Liu, Z., Zhu, L., Song, Z., 2014, Biochars derived from various crop straws: Characterization and Cd(II) removal potential, Ecotoxicology and Environmental Safety, 106, 226-231.

Tan, X.-f., Liu, Y.-g., Gu, Y.-l., Xu, Y., Zeng, G.-m., Hu, X.-j., Liu, S.-b., Wang, X., Liu, S.-m., Li, J., 2016, Biochar-based nano-composites for the decontamination of wastewater: A review, Bioresource Technology, 212, 318-333.

Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., 2015, Application of biochar for the removal of pollutants from aqueous solutions, Chemosphere, 125, 70-85.

Thirumavalavan, M., Lai, Y.-L., Lin, L.-C., Lee, J.-F., 2010, Cellulose-based native and surface modified fruit peels for the adsorption of heavy metal ions from aqueous solution: Langmuir adsorption isotherms, Journal of Chemical & Engineering Data, 55, 3, 1186-1192.

Tounsadi, H., Khalidi, A., Abdennouri, M., Barka, N., 2015, Biosorption potential of *Diplotaxis harra* and *Glebionis coronaria* L. biomasses for the removal of Cd(II) and Co(II) from aqueous solutions, Journal of Environmental Chemical Engineering, 3, 2, 822-830.

Tsai, W. T.,Chen, H. R., 2013, Adsorption kinetics of herbicide paraquat in aqueous solution onto a low-cost adsorbent, swine-manure-derived biochar, International Journal of Environmental Science and Technology, 10, 6, 1349-1356.

REFERENCES (continued)

Tursun, N., Akinci, I. E., Uludag, A., Pamukoglu, Z., Gozcu, D., 2012, Critical period for weed control in direct seeded red pepper (*Capsicum annum* L.), Weed Biology and Management, 12, 2, 109-115.

Uchimiya, M., Lima, I. M., Thomas Klasson, K., Chang, S., Wartelle, L. H., Rodgers, J. E., 2010, Immobilization of heavy metal ions (Cu^{II}, Cd^{II}, Ni^{II}, and Pb^{II}) by broiler litter-derived biochars in water and soil, Journal of Agricultural and Food Chemistry, 58, 9, 5538-5544.

Veera, S., 2013, The Use of Teabags Containing Indian Banana Peel Powder for Removal of Toxic Metal Ions from Drinking Water, Thesis, Lamar University, s.

Veglio, F.,Beolchini, F., 1997, Removal of metals by biosorption: a review, Hydrometallurgy, 44, 3, 301-316.

Vemula, P. K., 2012, The removal of toxic metal ions from drinking water by using tea bags containing bio-waste materials, Thesis, Lamar University-Beaumont, s.

Verheijen, F., Jeffery, S., Bastos, A. C., Van der Velde, M., Diafas, I. (2010). Biochar Application to Soils A Critical Scientific Review

of Effects on Soil Properties, Processes and Functions. Ispra, Italy, Institute for Environment and Sustainability**:** 162.

Verma, A., Kumar, S., Kumar, S., 2016, Biosorption of lead ions from the aqueous solution by *Sargassum filipendula*: Equilibrium and kinetic studies, Journal of Environmental Chemical Engineering, 4, 4, Part A, 4587-4599.

Vieira, R. H.,Volesky, B., 2000, Biosorption: a solution to pollution?, International Microbiology, 3, 1, 17-24.

Vijayaraghavan, K., 2016, Biosorption of metals: a complete handbook, 1st edition, Vinanie Publishers, India, p.219.

Vijayaraghavan, K.,Balasubramanian, R., 2015, Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions, Journal of Environmental Management, 160, 283-296.

Vijayaraghavan, K., Rangabhashiyam, S., Ashokkumar, T., Arockiaraj, J., 2017, Assessment of samarium biosorption from aqueous solution by brown macroalga *Turbinaria conoides,* Journal of the Taiwan Institute of Chemical Engineers, 74, 113-120.

REFERENCES (continued)

Vijayaraghavan, K.,Yun, Y.-S., 2008, Bacterial biosorbents and biosorption, Biotechnology Advances, 26, 3, 266-291.

Vimala, R.,Das, N., 2009, Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: A comparative study, Journal of Hazardous Materials, 168, 1, 376-382.

Viraj Gunarathne, A. A., Maneesha Prasaad Ginige, Shashikala Dilrukshi Premarathna, Ajith de Alwis, Bandunee Athapattu, Anushka Upamali Rajapaksha, and Meththika Vithanage, 2017, Municipal Waste Biochar for Energy and Pollution Remediation, Green adsorbents for pollutant removal, Grégorio Crini, E. Lichtfouse (Eds.), p. 227-252.

Volesky, B., 1990, Removal and recovery of heavy metals by biosorption, Biosorption of heavy metals, B. Volesky (Ed.), p. 7-43.

Volesky, B., 1999, Biosorption for the Next Century, Process Metallurgy, R. Amils, A. Ballester (Eds.), Elsevier, p. 161-170.

Volesky, B., 2001, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy, 59, 2, 203-216.

Volesky, B., 2003, Sorption and biosorption, BV Sorbex.

Volesky, B., 2007, Biosorption and me, Water Research, 41, 18, 4017-4029.

Wan, S., Wu, J., Zhou, S., Wang, R., Gao, B., He, F., 2018, Enhanced lead and cadmium removal using biochar-supported hydrated manganese oxide (HMO) nanoparticles: Behavior and mechanism, Science of the Total Environment, 616-617, 1298-1306.

Wang, G., Zhang, J., Shao, J., Liu, Z., Wang, H., Li, X., Zhang, P., Geng, W., Zhang, G., 2016, Experimental and modeling studies on CO2 gasification of biomass chars, Energy, 114, 143-154.

Wang, H., Gao, B., Fang, J., Ok, Y. S., Xue, Y., Yang, K., Cao, X., 2018a, Engineered biochar derived from eggshell-treated biomass for removal of aqueous lead, Ecological Engineering, 121, 124-129.

Wang, H., Gao, B., Wang, S., Fang, J., Xue, Y., Yang, K., 2015, Removal of Pb(II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from $KMnO_4$ treated hickory wood, Bioresource Technology, 197, 356-362.

REFERENCES (continued)

Wang, J.,Chen, C., 2009, Biosorbents for heavy metals removal and their future, Biotechnology Advances, 27, 2, 195-226.

Wang, J.,Wang, S., 2019, Preparation, modification and environmental application of biochar: A review, Journal of Cleaner Production, 227, 1002-1022.

Wang, L., Wang, Y., Ma, F., Tankpa, V., Bai, S., Guo, X., Wang, X., 2019, Mechanisms and reutilization of modified biochar used for removal of heavy metals from wastewater: A review, Science of the Total Environment, 668, 1298-1309.

Wang, Q., Wang, B., Lee, X., Lehmann, J., Gao, B., 2018b, Sorption and desorption of Pb(II) to biochar as affected by oxidation and pH, Science of the Total Environment, 634, 188-194.

Wang, T., Li, C., Wang, C., Wang, H., 2018c, Biochar/MnAl-LDH composites for Cu (II) removal from aqueous solution, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 538, 443-450.

Wani, A. L., Ara, A., Usmani, J. A., 2015, Lead toxicity: a review, Interdisciplinary Toxicology, 8, 2, 55-64.

Weber, K.,Quicker, P., 2018, Properties of biochar, Fuel, 217, 240-261.

Weber, W. J.,Morris, J. C., 1963, Kinetics of adsorption on carbon from solution, Journal of the Sanitary Engineering Division, 89, 2, 31-60.

Wei, D., Ngo, H. H., Guo, W., Xu, W., Du, B., Khan, M. S., Wei, Q., 2018, Biosorption performance evaluation of heavy metal onto aerobic granular sludge-derived biochar in the presence of effluent organic matter via batch and fluorescence approaches, Bioresource Technology, 249, 410-416.

Wilk, M.,Magdziarz, A., 2017, Hydrothermal carbonization, torrefaction and slow pyrolysis of *Miscanthus giganteus*, Energy, 140, 1292-1304.

World Health Organization, G., 1988, Environmental health criteria 61, World Health Organization, Geneva.

Xu, G., Yang, X., Spinosa, L., 2015, Development of sludge-based adsorbents: Preparation, characterization, utilization and its feasibility assessment, Journal of Environmental Management, 151, 221-232.

REFERENCES (continued)

Xu, X., Cao, X., Zhao, L., 2013, Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: Role of mineral components in biochars, Chemosphere, 92, 8, 955-961.

Xue, Y., Gao, B., Yao, Y., Inyang, M., Zhang, M., Zimmerman, A. R., Ro, K. S., 2012, Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests, Chemical Engineering Journal, 200-202, 673-680.

Yan, J., Xue, Y., Long, L., Zeng, Y., Hu, X., 2018, Adsorptive removal of As (V) by crawfish shell biochar: batch and column tests, Environmental Science and Pollution Research, 25, 34, 34674-34683.

Yang, J.,Volesky, B., 1999, Modeling uranium-proton ion exchange in biosorption, Environmental Science & Technology, 33, 22, 4079-4085.

Yao, Z., You, S., Ge, T., Wang, C.-H., 2018, Biomass gasification for syngas and biochar co-production: Energy application and economic evaluation, Applied Energy, 209, 43-55.

Yee, N., Benning, L. G., Phoenix, V. R., Ferris, F. G., 2003, Characterization of metal− cyanobacteria sorption reactions: a combined macroscopic and infrared spectroscopic investigation, Environmental Science & Technology, 38, 3, 775-782.

Yin, W., Guo, Z., Zhao, C., Xu, J., 2019, Removal of Cr(VI) from aqueous media by biochar derived from mixture biomass precursors of *Acorus calamus Linn.* and feather waste, Journal of Analytical and Applied Pyrolysis, 140, 86-92.

Yu, H., Pang, J., Ai, T., Liu, L., 2016, Biosorption of Cu^{2+}, Co^{2+} and Ni^{2+} from aqueous solution by modified corn silk: Equilibrium, kinetics, and thermodynamic studies, Journal of the Taiwan Institute of Chemical Engineers, 62, 21-30.

Yu, K. L., Lau, B. F., Show, P. L., Ong, H. C., Ling, T. C., Chen, W.-H., Ng, E. P., Chang, J.-S., 2017, Recent developments on algal biochar production and characterization, Bioresource Technology, 246, 2-11.

Yuvaraja, G., Krishnaiah, N., Subbaiah, M. V., Krishnaiah, A., 2014, Biosorption of Pb(II) from aqueous solution by *Solanum melongena* leaf powder as a low-cost biosorbent prepared from agricultural waste, Colloids and Surfaces B: Biointerfaces, 114, 75-81.

Zhang, D., Li, W., Zhang, S., Liu, M., Zhao, X., Zhang, X., 2011, Bacterial Community and Function of Biological Activated Carbon Filter in Drinking Water Treatment, Biomedical and Environmental Sciences, 24, 2, 122-131.

REFERENCES (continued)

Zhang, D., Luo, Q., Gao, B., Chiang, S.-Y. D., Woodward, D., Huang, Q., 2016a, Sorption of perfluorooctanoic acid, perfluorooctane sulfonate and perfluoroheptanoic acid on granular activated carbon, Chemosphere, 144, 2336-2342.

Zhang, J., Shao, J., Jin, Q., Li, Z., Zhang, X., Chen, Y., Zhang, S., Chen, H., 2019a, Sludge-based biochar activation to enhance Pb(II) adsorption, Fuel, 252, 101-108.

Zhang, L.-y., Zhu, X.-j., Sun, H.-w., Chi, G.-r., Xu, J.-x., Sun, Y.-l., 2010, Control synthesis of magnetic Fe3O4–chitosan nanoparticles under UV irradiation in aqueous system, Current Applied Physics, 10, 3, 828-833.

Zhang, Q., Li, Q., Zhang, L., Yu, Z., Jing, X., Wang, Z., Fang, Y., Huang, W., 2017a, Experimental study on co-pyrolysis and gasification of biomass with deoiled asphalt, Energy, 134, 301-310.

Zhang, X., Zhang, X., Chen, Z., 2017b, Biosorption of Cr (VI) from aqueous solution by biochar derived from the leaf of *Leersia hexandra* Swartz, Environmental Earth Sciences, 76, 2, 67.

Zhang, X., Zhao, X., Wan, C., Chen, B., Bai, F., 2016b, Efficient biosorption of cadmium by the self-flocculating microalga *Scenedesmus obliquus* AS-6-1, Algal Research, 16, 427-433.

Zhang, Z.-b., Cao, X.-h., Liang, P., Liu, Y.-h., 2013, Adsorption of uranium from aqueous solution using biochar produced by hydrothermal carbonization, Journal of Radioanalytical and Nuclear Chemistry, 295, 2, 1201-1208.

Zhang, Z., Zhu, Z., Shen, B., Liu, L., 2019b, Insights into biochar and hydrochar production and applications: A review, Energy, 171, 581-598.

Zhao, T., Yao, Y., Li, D., Wu, F., Zhang, C., Gao, B., 2018, Facile low-temperature one-step synthesis of pomelo peel biochar under air atmosphere and its adsorption behaviors for Ag(I) and Pb(II), Science of the Total Environment, 640-641, 73-79.

Zhou, K., Li, X., Li, J., Liu, M., Dang, S., Wang, D., Xin, X., 2015a, A clinical randomized controlled trial of music therapy and progressive muscle relaxation training in female breast cancer patients after radical mastectomy: Results on depression, anxiety and length of hospital stay, European Journal of Oncology Nursing, 19, 1, 54-59.

Zhou, K., Yang, Z., Liu, Y., Kong, X., 2015b, Kinetics and equilibrium studies on biosorption of Pb(II) from aqueous solution by a novel biosorbent: *Cyclosorus interruptus*, Journal of Environmental Chemical Engineering, 3, 3, 2219-2228.

REFERENCES (continued)

Zhou, N., Chen, H., Xi, J., Yao, D., Zhou, Z., Tian, Y., Lu, X., 2017, Biochars with excellent Pb(II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization, Bioresource Technology, 232, 204-210.

Zhou, Y., Zhang, L., Cheng, Z., 2015c, Removal of organic pollutants from aqueous solution using agricultural wastes: A review, Journal of Molecular Liquids, 212, 739-762.

Zubair, A., Bhatti, H. N., Hanif, M. A., Shafqat, F., 2008, Kinetic and equilibrium modeling for Cr (III) and Cr (VI) removal from aqueous solutions by *Citrus reticulata* waste biomass, Water, Air, & Soil Pollution, 191, 1-4, 305-318.